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EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE.
COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE
Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor. By Andrew A. Blair and J. Edward Whitfield.... 747
The Ferrates. By Claude A. O. Rosell..... 760
A Simple and Convenient Apparatus for Estimating the Water-holding Power of Soils. By J. L. Beeson..... 769
A Modification of Hinman's Explosion Pipette. By Augustus H. Gill..... 771
Estimation of Sulphur in Pyrites. By G. Lunge..... 772
The Periodides. By A. B. Prescott..... 775
An Improved Gas Regulator. By F. P. Dunnington..... 781
Inspection of Cotton for Use in the Manufacture of Guncotton. By Charles E. Munroe..... 783
Reduction with Magnesium Amalgam. By Hermann Fleck and Lewis L. Bassett..... 789
Two Definite Carbides of Iron with Chromium (Molybdenum and Tungsten). By James S. de Benneville..... 791
On the Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere. By Francis C. Phillips..... 801
A New Generator. By Edward P. Harris..... 809
The Determination of Tannin by Metallic Oxides. By William H. Krug..... 811
The Estimation of Sulphur in Refined Copper. By G. L. Heath.... 814
Acidimetric Estimation of Vegetable Alkaloids. By Lyman F. Kebler 822
New Books: Elements of Modern Chemistry; Justus Von Liebig, His Life and Work..... 832
Note: Determination of Acetic Acid in Vinegar..... 834

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PAPERS ACCEPTED FOR PUBLICATION:

An Early American Arrangement of the Elements. By F. P. Venable.
The Chlorides of Zirconium. By F. P. Venable.
Tellurium; Its separation from Copper Residues with Notes on some new Reactions. By Cabell Whitehead.
The Evolution Method for the Determination of Sulphur in White Cast Iron. By Francis C. Phillips.
Reactions between Copper and Concentrated Sulphuric Acid. By Chas. Baskerville.
On Silicates of Iron. By G. de Chalmot.
The Determination of Graphite in Pig-Iron. By P. W. Shimer.
Index to the Literature of the Detection and Estimation of Fusel Oil in Spirits. By W. D. Bigelow.
An Electric Process for the Manufacture of White Lead. By R. P. Williams.
Periodides of Pyridine. By A. B. Prescott and P. F. Trowbridge.
The Analysis of Alloys of Lead, Tin, Antimony, and Arsenic. By Lancelot Andrews.
The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture. By Arthur A. Noyes and Willard H. Watkins.
The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solution. By Arthur A. Noyes and John T. Dorrance.
The Determination of the Heating Effect of Coals. By W. A. Noyes, J. R. McTaggart and H. W. Craver.
On the Physical and Chemical Properties of Some California Oils. By Walter C. Blasdale.
On the Estimation of the Extraction in Sugar-Houses. By M. Trubek.
Arsenic in Glycerol. By G. E. Barton.

Issued with October Number, 1895

Proceedings.

ELEVENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

MINUTES:

The Eleventh General Meeting of the American Chemical Society was held in Springfield, Mass., August 27 and 28, 1895.

The meeting was called to order in Evangelist Hall, at 10 A. M., August 27, by the President, Professor Edgar F. Smith of Philadelphia.

President Smith introduced Mayor Charles L. Long, of Springfield, who spoke a few words of welcome to the Society, as follows:

"Mr. President and Members of the American Chemical Society. I cannot claim that the words I shall speak to you will rise to the dignity of an address. It was suggested to me that I should welcome the Society to Springfield, and this I most cordially do.

This is an occasion of great interest to our people. Nothing like it has occurred since the meeting of the American Association for the Advancement of Science here in 1859. You have met as the representatives of a great branch of science.

If I were called upon to name that branch of science that has accomplished the most practical results for mankind, I should say chemistry. The debt of gratitude that humanity owes to chemistry can never be repaid. Look at the results it has secured. Take for example, the Chemistry of Agriculture, it has made the earth to yield bountiful harvests. Then, too, the matter of foods and the preparation of foods for human consumption. Chemistry has given to the world the means for detecting the adulteration of foods. There is hardly an article that forms the dress of man or woman that does not owe its value to the skill of the chemist. In medicine, chemistry has done great service to man in providing cures for the various ills of the human body. For this mankind cannot be too grateful.

When the sun has set beyond the western hills and darkness has come on, you will find that the chemist has turned night into daylight in giving us the products of petroleum and illuminating gas, whether obtained from the destructive distillation of coal, or by the decomposition of steam. And so throughout the realm of human wants.

Why, then, should I not welcome to the city of Springfield, the representatives of a branch of science to which mankind is indebted more than to any other of the various branches of science? I trust your stay will be pleasant and that your deliberations will be profitable, and that after partaking of the hospitalities here, you will safely return to your respective homes."

President Smith, in behalf of the Society, replied:

"Mr. Mayor: In response to your very cordial invitation to come and take possession of the land, as it were, permit me to return the hearty thanks of the Society. We anticipate much pleasure and profit in our visit to this progressive city, known throughout the land as the place where so many scientific appliances are utilized. We shall gladly avail ourselves of the opportunities you offer.

In bidding us welcome to your city, you introduce to your fellow citizens the representatives of the youngest national chemical society, national in that its representatives are found in the east, the west, the north and the south. In recent years, also, the names of prominent European chemists have appeared upon our roll. Our object is to bring together all who cultivate the science of chemistry. In our membership of about one thousand, there are found many engaged in agriculture, in botany, in the iron industry, in coloring, and last but not least, the ubiquitous teacher of chemistry.

This Society fosters research, research not only in one direction, but in all. We have chemists interested in every department of chemistry. In this respect the American Chemical Society is unique, it stands alone. The great object of this Society is to make the science of chemistry in every way helpful to our fellow men.

Permit me, in advance, to thank you for the many hospitalities of which we shall be the recipients. We have nothing to offer in return unless you shall feel inclined to remain with us and listen to our papers and discussions."

At the conclusion of these remarks the President announced that the Society was ready for the presentation of papers and called upon Dr. W. A. Noyes, who read a paper on the "Determination of the Heating Effects of Coal," prepared by himself in conjunction with J. R. McTaggart and H. W. Craven. Dr. Noyes' paper was discussed by Drs. Hart and Prescott, after which Prof. F. P. Venable presented a paper entitled "A Case of Mistaken Identity." There was a short discussion on the paper by Drs. Hart and Prescott and President Smith, followed by a few remarks by the author.

The next paper was upon "The Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere," by Prof. Francis C. Phillips. This was discussed by Drs. W. A. Noyes, Edward Hart and E. E. Smith. Then R. P. Williams presented a paper on "A new Electrical Process for Making White Lead," which was discussed by Messrs. Meyers, Prescott, Hart, E. F. Smith and T. H. Norton.

Dr. A. A. Noyes read a paper on "The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solutions," and this was followed by another paper by the same author on "The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture." There were some discussions and questions on the last paper by Messrs. W. A. Noyes and A. B. Prescott, and a brief reply by the author.

An informal report of the present condition of the Society was given by the General Secretary, who announced the establishment of two local sections since the last meeting, one in Nebraska, with headquarters at Lincoln, Nebr., and the other in the city of Chicago. The membership of the Society was stated to be just 900. There are also some persons who have been elected but have not yet qualified, and quite a number of persons whose applications for membership have been favorably reported by the Standing Committe on Nominations to membership, so that practically the number of members may be considered as about 950.

The following named members have died since the report given at the last General Meeting:

Dr. A. A. Fesquet, Dec. 26, 1894.
Prof. H. B. Nason, Jan. 17, 1895.
J. C. Dittrich, (drowned on the Elbe) Jan. 1895.
W. H. Whalen, Feb. 3, 1895.
Prof. Mark Powers, Mar. 1, 1895.
Lewis Hoffman, Mar. 4, 1895.
Dr. Gideon E. Moore, April 15, 1895.
W. G. Wallace, April, 1895.
Wm. C. Wilson, April 16, 1895.

There are now eight Local Sections of the Society; *viz.*, Rhode Island, Cincinnati, New York, Washington, Lehigh Valley, New Orleans, Nebraska and Chicago.

A bill was passed by the legislature of the State of New York during its last session, allowing the Society to elect its directors without regard to their residence or citizenship, and legalizing all action of the Society that may be taken at any of its meetings outside of the State of New York. Prof. F. W. Clarke, chairman of the committee appointed to consider the question of amendments to the constitution, has resigned, and Dr. H. W. Wiley has been appointed to fill the vacancy.

After the report by the General Secretary and certain announcements regarding excursions, visits, and sessions of the Society, a paper on "The Determination of Sulphur in Refined Copper," by George L. Heath, was read by Dr. Wm. McMurtrie, the author being absent. The morning session was then adjourned.

In the afternoon the chemists made an excursion to Holyoke, leaving Springfield at 1 P. M. and returning in time for the evening session. At Holyoke they visited the mills of the Holyoke Paper Company, the Merrick Thread Company, and the Farr Alpaca Company.

At 1 P. M. under the guidance of Messrs. H. H. Bosworth, C. M. Kirkham, J. Eastman Belding and H. S. Anderson of the Local Committee, the chemists took the electric car for Holyoke. They visited first the mills of the Holyoke Paper Company. Mr. Oscar Greenleaf, Treasurer of the Company, conducted the party through the building and explained to them very clearly and minutely the various steps in the manufacture of paper from the beginning to the end.

The company use both American and foreign rags. The rags are first dusted in a star-shaped holder, which, by its revolution, allows the rags to fall down from one star-point to another thus driving out the dust which escapes through the meshes of the sieve-like sides of the holder.

After being dusted the rags are placed upon tables where they are picked over by hand, and buttons, hooks and eyes, pieces of whalebone, rubber, etc., are removed, scythes being used to cut them off when possible. Sometimes valuable articles are found and these the workers are allowed to keep. This furnishes a valuable incentive for the careful examination of the rags. After the first picking-over the rags are examined again by another person and any remaining objectionable articles removed, and the rags are also sorted into different grades. The rags are then passed between closely fitting cogs which tear them into shreds,

after which they are chopped into small pieces by an instrument in which the knives revolve in a manner similar to those of a lawn mower. After this the rags are sometimes subjected to another process of dusting by being whipped while in a suitable receptacle.

They are then put into large revolving cylinders and boiled under pressure of thirty-five to fifty pounds in milk of lime of about the consistency of cream. After being thus treated sufficiently they are removed, the lime allowed to drain off, and the rags are then put into washing engines, where they are reduced to pulp, a stream of clear spring water flowing in and a stream of dirty water flowing out continuously at the other end of the washing machine.

The rags are reduced to pulp by the scraping action of steel bars, those of one set passing through the narrow spaces between the others and thus drawing out the fiber somewhat like the process of scraping cloth for lint. When the rags have been reduced to pulp and sufficiently washed, a solution of chloride of lime is run in for the purpose of bleaching the pulp. At this stage the flow of water in and out of the vat is checked, as is also the pulp-reducing action of the machine, and the mechanical action is simply such as to keep the bleaching pulp stirred and rotating around in the vat of the machine.

After being bleached the pulp is allowed to flow into draining rooms, *i. e.*, into large receptacles containing a perforated bottom, where it remains from five days to three or four weeks, according to the requirements. The chloride-of-lime water is there drained off.

The bleached and drained pulp is then put into beating engines, where it is washed with water to remove any remaining chloride of lime, and if necessary, sodium hyposulphite is added to neutralize the last traces of the chloride. It is here reduced to a very fine fiber. Then it is put into a large tank and pumped on to a paper machine having a large endless piece of wire cloth, which is drawn along and carries with it the fiber thinned with a sufficient amount of water. In this operation the cloth is given a shaking motion, and as the water runs off the fibers are shaken closely together, interlaced more or less, and packed down so as to cohere into one continuous sheet. The remaining water, so far as possible, is withdrawn from the fiber by a suction pump.

From the wire cloth the paper passes between heavy rollers and upon a sheet of woolen felt. Thence it goes over iron cylinders heated inside with steam. After the paper is thus dried, it is passed through a solution of glue or extract of rawhide. This animal sizing is thus absorbed by the paper, some vegetable sizing having been already introduced into the material in the beating engine. The vegetable sizing is resin. The paper, wet with animal sizing, is hung over poles where it dries slowly. If rapidly dried, the strength of the glue is partly destroyed.

When dried, the paper is calendered. There are two methods of calendering: (1) the American, by which the paper passes between rolls,

three of chilled iron and two of paper arranged alternately; (2) the foreign, by which the paper is pressed between two heavy chilled rolls after having been packed in layers between zinc or pasteboard plates.

The best quality of paper is not weighted. No weighting is done at the mills of the Holyoke Paper Co. Whenever weighting is done at all, the weighting—or filling—material is introduced into the heating engines with the pulp.

Mr. O. S. Greenleaf, Treasurer of the Holyoke Paper Co., in addition to his other many courtesies, sent to the General Secretary a package containing a sample box of paper and envelopes for each of the chemists who had visited their mill. These were not received until after the adjournment of the meeting and some of the chemists had left the city, but the boxes were distributed to all who were still accessible and the General Secretary, in behalf of the members, sent a letter to Mr. Greenleaf, expressing their cordial thanks for this pleasing souvenir of their visit.

The evening session on Tuesday, Aug. 27, was held in room 6 of the High School, President E. F. Smith presiding. A paper upon "The Speed of Oxidation by Chloric Acid," prepared by Dr. R. B. Warder and Herman Schlundt, was read by Dr. Warder and afterwards discussed by Drs. Norton, A. A. Noyes and Warder. This was followed by a paper on "The Reaction between Copper and Concentrated Sulphuric Acid," by Chas. Baskerville. The subject of Mr. Baskerville's paper was discussed by Dr. Andrews, after which a few words of reply were offered by the author.

The closing paper of the evening session was read by Prof. Francis C. Phillips. The subject of the paper was, "The Evolution Method for the Determination of Sulphur in Iron." After the reading of the paper the subject was discussed by Dr. Hart, and then after some announcements by the Secretary, the evening session was adjourned.

The Society assembled for its morning session Aug. 28, at 9 A. M. in Evangelist Hall, President Smith in the chair. Dr. Norton read a paper upon "The Use of Aluminum for Condensers," and this was discussed by Drs. Hale, McMurtrie and others. A paper upon "Arsenic in Glycerol," prepared by Geo. E. Barton, was read by Dr. McMurtrie in the absence of the author. The subject was discussed by Messrs. Prescott, W. P.

Mason and Munsell. Then followed a paper presented by Mr. Lyman F. Kebler on "The Acidimetric Estimation of Vegetable Alkaloids." This paper elicited considerable discussion, the following named gentlemen taking part: Messrs. Prescott, W. A. Noyes, Sabin, W. P. Mason, Bigelow, Munsell, Andrews and Kebler.

The next paper was upon "Metaphosphinic Acids and their Derivatives," by Henry N. Stokes, and a few remarks were made upon this paper by Dr Norton. Chas. H. Herty then presented a paper on "Observations on Double Platinum Salts." This was discussed by Messrs. Stokes, Howe, W. P. Mason and Myers, after which Dr. Launcelot W. Andrews read a paper on "The Analysis of Alloys containing Tin, Lead and Antimony.

After the General Secretary had made some announcements, Wm. K. Robbins described a new burette holder, designed by himself, and Dr. A. A. Noyes announced the publication of the "Review of American Chemical Research," and distributed specimen pages of the periodical to the members present. Prof. W. P. Mason described a new kind of water-bath. Dr. Hart, in the absence of the author, read a paper upon "Tellurium, its Separation from Copper Residues, with Notes on some New Reactions," prepared by Cabell Whitehead.

President Smith then invited Prof. E. W. Morley, President of the American Association for the Advancement of Science, to address the Society. Dr. Morley in reply made some informal remarks, summing up the results of investigations that have been made upon the "Atomic Weight of Oxygen," which, by any reasonable system of averaging the results of all of the most reliable investigations, was shown to be 15.879. President Smith thanked Prof. Morley very heartily for his remarks, and in most complimentary terms showed how the chemists of America are to be congratulated upon having among their number, one whose own research upon the atomic weight of oxygen would rank among the most profound and reliable investigations that have ever been made upon that subject by any scientist of any country.

Dr. A. B. Prescott said, "I can add nothing to the words

already spoken in congratulation to this Society and to this meeting, words most fit to be spoken at this time, in all of which I desire most sincerely to join. If I would add another word to express what has been in my heart as we sat here, it would be a word of acknowledgment for us all, of what we owe to our presiding officer in this meeting. He has conducted our discussions with equal interest and spirit in all subjects, suggesting fruitful inquiry and saving the valuable time of the meeting, crowded as it has been with papers and living topics. I am sure I can speak for every member of the Society in giving thanks to both the General Secretary and the President for their tireless and effective service in preparing for this meeting and conducting it throughout."

Drs. Hart and Norton followed briefly with similar remarks, and upon motion of Dr. Hart, the Society passed a vote of thanks to the President and General Secretary in harmony with the sentiments that had just been expressed.

Upon motion of the General Secretary the thanks of the Society were extended to the Local Committee of Arrangements in Springfield for their untiring efforts to make the meeting of the chemists a pleasant and successful one, and especially to the Local Secretary, Mr. Wm. A. Webster. Also to Prof. Wm. Orr, Jr., Chairman, and Mr. Henry H. Bosworth, Secretary of the Committee on Excursions; to Mr. C. M. Kirkham, Mr. J. Eastman Belding, and Mr. H. S. Anderson; to the officers of the Holyoke Paper Company for permission to visit their mills and to Mr. O. S. Greenleaf, Treasurer of said Company, and Mr. C. J. Humeston; to the Farr Alpaca Company, and especially to Mr. H. M. Farr, Agent, and Mr. F. H. Metcalf, Superintendent; to the Merrick Thread Company, and especially to Mr. O. H. Merrick, Superintendent, and Mr. S. M. Bentley; to the United Electric Light Company, the Hampden Paint and Chemical Company, and to the officers in charge of the United States Armory, especially to Col. Alfred Mordecai, Major W. H. Rexford and Lieut. Tracy C. Dickson, for their personal and official courtesies; to the hotels and railroad companies for reduced rates; to the local press for their careful and complete reports of the meeting, and to the citizens of Springfield generally for their many

hospitalities and their efforts to make our visit to their city pleasant and our meeting successful.

The remaining visits to be made by the chemists were announced, after which the Eleventh General Meeting of the Society was formally adjourned.

According to the announcements made the members visited the United States Armory and the Hampden Paint and Chemical Works during the afternoon, and early the following morning those who cared to go were very courteously received at the plant of the United Electric Light Company by Mr. H. S. Anderson, electrician, who conducted them through the works and showed them many very interesting experiments with high tension currents. This formed a very fitting termination of one of the most enjoyable and successful meetings the Society has ever held.

The following members registered in attendance at the meeting:

Edgar F. Smith, Philadelphia, Pa.
Albert C. Hale, Brooklyn, N. Y.
Wm. McMurtrie, Brooklyn, N. Y.
Edward Hart, Easton, Pa.
Wm. Bromwell, Port Deposit, Md.
W. D. Bigelow, Washington, D. C.
A. H. Sabin, New York.
Wm. Frear, State College, Penna.
Francis C. Phillips, Western Univ., Allegheny, Pa.
Rufus P. Williams, English High School, Boston.
Robt. B. Warder, Washington, D. C.
Frank N. Guild, Greensboro, Vt.
A. F. Linn, Wittenberg College, Springfield, O.
Fred. W. Morse, N. H. Expt. Sta., Durham, N. H.
Arthur A. Noyes, Mass. Inst. of Tech., Boston, Mass.
J. A. Deghuee, Brooklyn, N. Y.
W. A. Noyes, Terre Haute, Ind.
Mary Engle Pennington, Philadelphia, Penna.
Elizabeth A. Atkinson, Three Tuns, Penna.
E. W. Allen, Washington, D. C.
Alfred H. Mason, New York.
J. B. Lindsey, Amherst, Mass.
A. B. Prescott, Ann Arbor, Mich.
F. P. Venable, Chapel Hill, N. C.
Ernest Ellsworth Smith, New York.

Frank D. Maine, Springfield, Mass.
Otis C. Johnson, Ann Arbor, Mich.
Thomas H. Norton, Cincinnati, O.
Chas. Baskerville, Chapel Hill, N. C.
J. Bird Moyer, Univ. of Penna., Philadelphia.
C. Smith Boynton, Burlington, Vt.
B. B. Ross, Auburn, Ala.
B. W. Kilgore, Raleigh, N. C.
Francis E. Bates, Westfield, ——.
John A. Myers, Morgantown, W. Va.
Charles L. Parsons, Durham, N. H.
William P. Mason, Troy, N. Y.
Alfred Springer, Cincinnati, O.
Launcelot Andrews, Iowa City, Ia.
Lyman B. Hall, Haverford, Pa.
L. P. Strong, Springfield, Mass.
Leslie A. Cooper, Springfield, Mass.
Wm. Woodhouse, North Adams, Mass.
P. H. Rolfe, Lake City, Fla.
F. Atwood Sirrine, Jamaica (L. I.) N. Y.
Geo. W. DeWolf, Springfield, ——.
Chas. H. Herty, Athens, Ga.
Lyman F. Kebler, Philadelphia, Pa.
Charles E. Munsell, Brooklyn, N. Y.
T. R. White, New York.
George D. Gable, Fairfield, Iowa.
Jas. Lewis Howe, Washington and Lee Univ., Lexington, Va.
W. K. Robbins, Manchester, N. H.
H. N. Stokes, Washington, D. C.
Walter E. Smith, Providence, R. I.
W. O. Atwater, Middletown, Conn.
Charles E. Munroe, Washington, D. C.
Edward W. Morley, Cleveland, Ohio.
Mrs. E. F. Smith, Philadelphia, Pa.
E. D. Campbell, Ann Arbor, Mich.
Mary F. Leach, Mt. Holyoke College, S. Hadley, Mass.
Paul C. Freer, Ann Arbor, Mich.
Clara A. Pease, High School, Hartford, Conn.
Frank E. Coombs, Natick, Mass.
E. Twitchell, Cincinnati, O.

ALBERT C. HALE,
General Secretary.

NEW MEMBERS ELECTED SEPT. 21.

Ando, Shinichi, care of Apollo Iron and Steel Co., Apollo, Pa.
Carnell, Wm. C., lab. Ill. Steel Co., So. Chicago, Ill.
Crane, Wm. H., M.D., 92 W. 7th St., Cincinnati, O.
DeFremery, J. L., 44 Broadway, N. Y. City.
DeRoode, Rudolf, care of Fraser & Co., 262 5th Ave., N.Y. City.
DuPont, Francis G., Wilmington, Del.
Johnson, Jesse F., care of Hamilton Powder Co., Montreal, Can.
Macadam, Wm. Ivison, Surgeon's Hall, Edinburgh, Scotland.
Swett, Charles E., 23 Bolander St., Providence, R. I.
Thackray, George E., Cambria Iron Co., Johnstown, Pa.

ASSOCIATE ELECTED SEPT. 21.

Read, Frederick, 140 Nassau St., N. Y. City.

CHANGES OF ADDRESS.

Allen, W. N., 2 Chestnut St., Philadelphia, Pa.
Barton, G. E., Columbian Univ., Washington, D. C.
Brinker, Harry L., 811 West Federal St., Youngstown, O.
Chase, George W., Bellwood, Pa.
Dewey, F. P., 702 Ninth St., N. W., Washington, D. C.
Fuller, Fred D., 7 Dix St., Worcester, Mass.
Gudemann, Edw., Davenport, Iowa.
Hand, Daniel, Edison Lamp Works, Harrison, N. J.
Hershey, A. N., care of A. L. Thomsen, Mfg. Chemist, Baltimore, Md.
Hoffman, Philip C., care of Georgia Chemical Works, Augusta, Ga.
Innes, Murray, care of Old Dominion Copper Co., Globe, Arizona.
Lammers, Theodore L., Townsend, Montana.
Leighton, Virgil L., Tufts College, Mass.
Linebarger, C. E., 2601 Calumet Ave., Chicago, Ill.
Loeb, Dr. Morris, 112 N. 72d St., New York City.
Meeker, G. H., care of Andover Iron Co., Phillipsburg, N. J.
Mellen, E. D., 9A Forest St., N. Cambridge, Mass.
Peacock, S., care of Nolan Pub. Co., P. O. Box 2113, Philadelphia, Pa.
Pemberton, H., Jr., 2027 Spruce St., Philadelphia, Pa.
Puckner, W. A., 73 Wells St., Chicago, Ill.
Seamon, F. H., Apartado 101, Matehuala Est San Luis Potosi, Mexico.
Seher, August, 115 Chestnut St., Newark, N. J.
Trimble, Henry, 145 N. 10th St., Philadelphia, Pa.
Wesson, David, The Wesson-Nivison Mfg. Co., Cortlandt, N. Y.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The first meeting of the new year, 1895–96, was held at Providence, Thursday evening, Sept. 26, 1895. Prof. J. H. Appleton, of Brown University, gave an address on "Sugar and Sugar Refining," illustrated by about sixty slides shown by the lantern. Many of the slides were from negatives taken in remote sugar-producing countries, *e. g.*, Sandwich Islands, South Africa, and of course, Cuba.

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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

AMMONIUM PHOSPHOMOLYBDATE AND THE REDUCING ACTION OF ZINC IN THE REDUCTOR.

BY ANDREW A. BLAIR AND J. EDWARD WHITFIELD.

Received August 7, 1895.

AMONG the problems presented to the sub-committee on Methods of the International Steel Standards Committee, in the choice of a method for the determination of phosphorus in steel, none seemed more important than those involved in the composition of ammonium phosphomolybdate, and the reducing action of zinc on the molybdic acid of this salt under different conditions. The object of this investigation was to present data for the settlement of this question.

COMPOSITION OF AMMONIUM PHOSPHOMOLYBDATE.

In the preparation of ammonium phosphomolybdate the method usually followed was to precipitate the salt by adding a solution of microcosmic salt to a solution of ammonium molybdate in nitric acid; but Doolittle and Eavenson[1] showed that ammonium phosphomolybdate precipitated from a solution containing a large excess of ferric nitrate had essentially the same composition as that obtained by following the usual method of procedure.

In the investigation which we have made, we prepared a number of samples under different conditions and made careful analysis of each as a basis for our work.

[1] This Journal, 16, 234.

Sample 1.—Prepared by dissolving twenty grams of steel free from arsenic in nitric acid, adding twenty-five cc. of a saturated solution of microcosmic salt, evaporating to dryness, heating until the ferric nitrate was decomposed, dissolving in hydrochloric acid, diluting, filtering, evaporating to syrupy consistency, and then evaporating three times with excess of nitric acid to remove the hydrochloric acid. The solution was diluted to one liter, heated to about 60° C., and poured into one liter of molybdate solution. The precipitate was allowed to settle, the supernatant liquid was decanted, and the precipitate was washed by decantation with water containing one per cent. of nitric acid and finally filtered, washed, dried, removed from the filter, and heated to 150° C. for five hours.

Sample 2.—Prepared by partially neutralizing the first decantation from sample 1, adding twenty-five cc. more of the same microcosmic salt, washing, and drying the precipitate as above.

Sample 3.—Prepared by pouring a solution of microcosmic salt acidulated by nitric acid into molybdate solution, washing with water containing one per cent. of nitric acid, and filtering. A portion of this precipitate was dried at 150° C. for eight hours for sample 3.

Sample 4.—Prepared by taking a second portion of the precipitate above, washing with ice-water and drying over potassium hydroxide at the ordinary temperature for three months.

Sample 5.—Prepared by taking a third portion of the same precipitate, washing again with water containing one per cent. of nitric acid, and drying in the same manner as sample 4.

Sample 6.—The same as sample 5, but digested and washed before drying with water containing five per cent. of nitric acid.

Sample 7.—The same as sample 5, but digested and washed with water containing ten per cent. of nitric acid.

Sample 8.—Prepared by dissolving ferric oxide (obtained by igniting pure ferric oxalate) in hydrochloric acid, adding five per cent. of pure phosphoric anhydride, evaporating off the hydrochloric acid with nitric acid, heating to 80° C., adding an

excess of molybdate solution at 20° C., shaking in a large flask for three minutes and washing with water containing one per cent. of nitric acid. After thorough washing, the precipitate was digested with consecutive portions of water, containing varying amounts of nitric acid and with water containing nitric acid and ammonium nitrate. Then after standing two months with half a liter of water, containing five per cent. of nitric acid, it was filtered, washed with water containing five per cent. of nitric acid, and heated to 100° C. for five hours.

Sample 9.—Prepared from the same reagents, and in the same manner as sample 8. Washed by decantation with water containing five per cent. of nitric acid, dried at 100° C. for eight hours.

Sample 10.—Prepared and washed in the same manner as sample 9, but dried at 100° for twelve hours.

The methods employed in the analyses of these samples are the usual ones except that for the determination of water, and a general description will be sufficient.

As the salt is very hygroscopic the samples were in all cases placed in drying tubes with glass stoppers, heated to the temperature indicated, cooled over fused potassium hydroxide, and weighed out by difference.

DETERMINATION OF PHOSPHORIC AND MOLYBDIC ACIDS.

About two grams of the salt was weighed out by difference into a beaker, dissolved in twenty-five cc. of ammonia (0.96 sp. gr.) transferred to a carefully calibrated half liter flask and diluted to the mark with water. The solution was thoroughly mixed by pouring it into a dry beaker and back into the flask several times. By means of a pipette, which had been carefully tested against the flask, 100 cc. (containing about four-tenths gram of the salt) was measured into a beaker for the estimation of the molybdic acid, and 200 cc. (containing about eight-tenths gram of the salt) was measured into another beaker for the estimation of the phosphoric acid. To the latter was added, drop by drop, ten cc. of magnesia mixture with constant stir-

ring, then fifty cc. of ammonia and the precipitated ammonium magnesium phosphate was allowed to stand over night. The precipitate was filtered, washed with ammonia water, dissolved on the filter in dilute hydrochloric acid, made slightly alkaline with ammonia, ammonium sulphide added, the solution acidulated with hydrochloric acid and hydrogen sulphide passed through the hot solution for half an hour. The precipitated molybdenum sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide and the ammonium magnesium phosphate reprecipitated as before. This precipitate was filtered off, burned and weighed as magnesium pyrophosphate, and the phosphoric acid and phosphorus calculated in the usual way.

The solution for the determination of molybdic acid was diluted to about three-fourths of a liter with hot water, heated to boiling, slightly acidulated with acetic acid and a boiling solution of lead acetate (containing about three grams of the salt) was added. After boiling for about fifteen minutes the precipitate was allowed to settle, decanted through an asbestos filter on a Gooch crucible, washed thoroughly by decantation with hot water, transferred to the crucible, dried at 120° C., and weighed as the mixed lead phosphate and molybdate.

The percentage of the mixed salts was calculated and from this amount was subtracted the percentage of lead phosphate found by multiplying the percentage of phosphorus previously found by 13.086. The difference (lead molybdate) multiplied by 0.39242 gave the percentage of molybdic acid.

DETERMINATION OF AMMONIA.

About one and a half to two grams of the salt was weighed out into a funnel inserted in the neck of a fractional distillation flask and washed down into the flask with water. The flask was fitted with a stopper carrying a bulb tube with a glass stopcock. The side tube of the flask was fitted into a glass condenser to the lower end of which was attached one arm of a large bulb U tube containing ten cc. of hydrochloric acid and twenty cc. of water. The other arm of the U tube was fitted with a small calcium chloride tube, containing broken glass moistened with water. Fifty cc. of pure potassium hydroxide (1.27 sp.

gr.) was admitted to the distillation flask through the bulb tube, and the ammonia was distilled over. The contents of the U tube were transferred to a beaker, platinic chloride added, and the ammonia determined in the usual way.

DETERMINATION OF WATER.

The determination of water in ammonium phosphomolybdate offered unexpected difficulties. After repeated trials to get satisfactory results by heating the salt with sodium tungstate the following method was adopted:

At the middle point of a tube of hard glass 200 millimeters long, and nineteen millimeters in diameter was fused at right angles a tube thirty-seven millimeters long and nine millimeters in diameter. In the small tube a thermometer was fitted with sheet asbestos. The bulb of the thermometer extended a short distance into the large tube. The tube was placed in a horizontal position across the ring of an iron retort holder, the middle of it being protected by a piece of sheet copper three inches long bent around it, but separated from it by sheet asbestos. The ends of the tube were fitted with perforated corks, one carrying a small glass tube for the passage of dry air, and the other a U tube filled with calcium chloride. A porcelain boat sixty-two millimeters long and twelve millimeters wide was provided to hold the salt.

The stand holding the tube now closed with solid stoppers was placed near the balance case, about two grams of the salt was weighed out by difference into the boat which was immediately placed in the tube, and the latter closed by the corks. It was then placed in position, the perforated corks substituted for the others and a current of dry air passed through while the tube was heated by a Bunsen burner until the thermometer registered 250° C. The increase in weight of the calcium chloride tube gave the amount of water.

The only danger apprehended was that of decomposing the salt and liberating its ammonia, but careful experiments made by passing the air over the salt heated to 250° C. and into Nessler's solution showed that no trace of ammonia was given off.

The results of the analysis of the samples are as follows:

Sample.	Phosphoric acid. Per cent.	Molybdic acid. Per cent.	Ammonium oxide $(NH_4)_2O$. Per cent.	Water. Per cent.	Ratio of Phosphorus to 100 molybdic acid.
1	3.79	91.88	3.33	1.02	1.799
2	3.79	91.63	3.39	1.30	1.805
3	3.80	91.67	3.34	1.22	1.810
4	3.59	88.06	3.36	5.02	1.778
5	3.63	89.07	....	....	1.786
6	3.57	86.44	....	....	1.802
7	3.56	86.89	....	....	1.789
8	3.73	91.37	2.64	1.96	1.780
9	3.79	92.33	3.12	0.71	1.790
10	3.81	91.96	3.03	1.17	1.807
				Average for the ten samples,	1.7946

These results are sufficient to show remarkable uniformity in the composition of ammonium phosphomolybdate precipitated under varying conditions and may be considered as practically answering the question as to the effect of the presence of ferric nitrate in the solution from which the precipitation is effected.

There are two points worthy of remark in these results. First, the variation in the amounts of water in the different samples, and second. the variation in the amounts of ammonia.

The explanation of the first point is found probably in the temperature of drying, that of the second in the washing of the precipitated salt. Sample 8, which was digested for a long time with dilute nitric acid, had lost most ammonia. This is borne out by the fact that the ammonia can all be destroyed by digestion with aqua regia and phosphomolybdic acid crystallized out from the solution. In this connection the following table of calculated composition compared with results obtained by analysis may be of interest:

SAMPLE 10.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO_3	3456	91.19	91.96
P_2O_5	142	3.74	3.81
3 $(NH_4)_2O$	156	4.12	3.03
2 H_2O	36	0.95	1.17
	4790	100.00	99.97
Phosphorus ratio		1.794	1.807

SAMPLE 4.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO_3	3456	87.45	88.06
P_2O_5	142	3.59	3.59
3 $(NH_4)_2O$	156	3.95	3.36
22 H_2O	198	5.01	5.02
	3952	100.00	100.03
Phosphorus ratio		1.794	1.778

The last trace of water seems to go off between 150° and 250° C., but the samples having been prepared and analyzed after drying at or below 150° C it was not deemed necessary to prepare the anhydrous salt especially as it is very hygroscopic. In view of the fact that the variation in the ratio of molybdic acid to phosphorus is so small (the average of the ten samples being 1.7946) we may without hesitation adopt the theoretical ratio of 1.794.

Samples 4, 5, 6, and 7 were prepared to test the accuracy of the statement made by Hundeshagen[1] that the precipitated ammonium phosphomolybdate washed with dilute acid and dried in a desiccator over calcium chloride and potassium hydroxide had the composition

$$12MoO_3,\ P_2O_5,\ 3(NH_4)_2O,\ 4HNO_3,\ 2H_2O.$$

Actual tests of these samples made by dissolving weighed amounts in a standard solution of potassium hydroxide and titrating back with standard nitric acid gave the following results:

	Standard alkali required to neutralize one gram of salt.
No. 3	130.53
" 4	119.14
" 5	121.25
" 6	123.59

Sample 7 was unfortunately used up in the preliminary analysis and none remained for this test, but as No. 3 was heated to 150° C., and the others were dried as described above, No. 4 having been washed with water, No. 5 with one per cent. nitric acid, and No. 6 with five per cent. nitric acid the results do not seem to bear out Hundeshagen's statement.

[1] *Chem. News*, 60, 168.

It was hoped also, that the neutralization (Handy's) method might offer some advantages over the reduction method for the determination of phosphorus in steel, but the hygroscopic charactor of the ammonium phosphomolybdate and the lack of agreement in the results obtained caused us to abandon this part of the investigation.

THE REDUCTION OF MOLYBDIC ACID BY ZINC.

When a solution of ammonium phosphomolybdate in ammonia is acidulated with sulphuric acid and the molybdic acid is reduced by metallic zinc it was claimed by Wernicke that the reduction was not to the form Mo_2O_3 but to $Mo_{12}O_{19}$. This theory was adopted by Emmerton and has been generally accepted by chemists as the formula to be used in the determination of phosphorus by the reduction method. When Jones' reductor came into general use it was noticed that the green color of the reduced solution was more permanent and the oxidation with potassium permanganate was from this color and not from the port-wine color referred to by Emmerton. Babbitt[1] claimed that the reduction was to a point between Mo_2O_3 and $Mo_{12}O_{19}$ but Noyes[2] claimed that the reduction was to Mo_2O_3.

The reactions may be indicated as follows for the subsequent oxidation by potassium permanganate :

$$5Mo_{12}O_{19} + 17K_2Mn_2O_8 = 60MoO_3 + 17K_2O + 34MnO,$$
$$5Mo_{24}O_{37} + 35K_2Mn_2O_8 = 120MoO_3 + 35K_2O + 70MnO,$$
$$5Mo_2O_3 + 3K_2Mn_2O_8 = 10MoO_3 + 3K_2O + 6MnO,$$

then as

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O ;$$

or one molecule $K_2Mn_2O_8$ oxidizes ten molecules of iron to the ferric condition, and we have for the ratio of iron to molybdic acid 100 to 90.756 in the first case, to 88.163 in the second, and to 85.714 in the third.

In other words, we must multiply the value of the permanganate solution in iron by 0.90756, by 0.88163, or by 0.85714 according to the theory we adopt for the reducing action of zinc on the solution of ammonium phosphomolybdate.

[1] *J. Anal. Appl. Chem.* **7**, 165.
[2] This Journal, **16**, 553.

The differences are certainly too great to be disregarded, and it becomes necessary to decide which theory we must adopt.

We have, therefore, sought to discover in the following experiments, first, what conditions affect the reduction, and secondly, whether the methods in ordinary use are capable of giving uniform results.

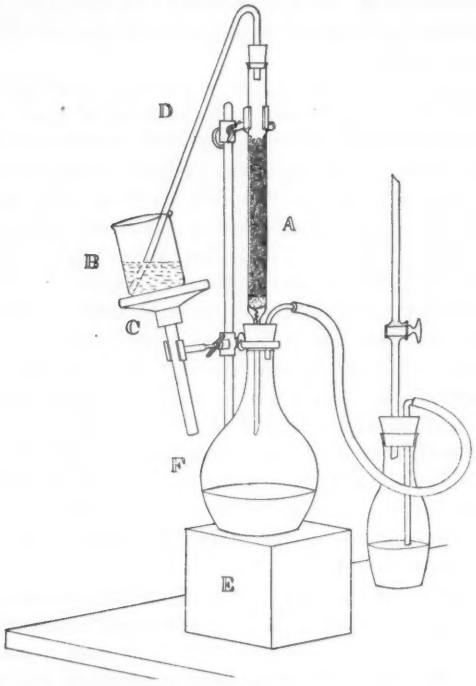
First, sample 10, containing 91.96 per cent. molybdic acid was selected for these experiments and a number of glass stoppered weighing tubes were filled with the carefully ground and dried salt. About two grams of the salt was weighed by difference into a beaker, dissolved in five cc. ammonia (0.96 sp. gr.) washed out into a half liter flask, diluted to the mark with distilled water, mixed by pouring back and forth into a dry beaker, and measured out by means of a twenty-five cc. pipette, carefully tested with the flask into beakers. Twenty cc. ammonia (0.96 sp. gr.) were added, the solution was acidulated with twenty-five cc. sulphuric acid (1–4) and passed through the reductor. The reduced solution was titrated with standard permanganate and the molybdic acid calculated by the proper formula.

The reductor shown in the accompanying sketch was used. This form of reductor was suggested by Mr. W. P. Barba of the Midvale Steel Co., a member of the sub-committee on Methods of the International Steel Standard Committee, and has been found most convenient.

In the bottom of the reductor tube A was placed a spiral of platinum wire, on top of this a piece of platinum gauze, a wad of glass wool six millimeters thick, and then a thin film of asbestos. The tube was filled with granulated zinc to within thirty-seven mm. of the top and a wad of glass wool twelve millimeters thick filling the diameter of the tube placed on top. This served to distribute the acid and to prevent the liberated hydrogen from spattering the solution on the upper part of the tube. The solution having been placed in the beaker B, the latter was placed on the stand C, and the tube D placed in position. The flask F having been attached, the block E was placed under it, and the pump having been connected the liquid was drawn over from B.[1] When the liquid in B was almost all

[1] See seq. for use of dilute sulphuric acid for washing.

drawn over, the sides of the beaker were washed down and then the beaker was filled with water, and when this was all drawn over, the stopper carrying the tube D was removed and the re-



ductor tube was filled with water to thoroughly wash out the top of the tube. The flask was removed, the end of the reductor tube washed into it, the sides of the neck of the flask washed down with water, and the reduced liquid was titrated in the flask.

In making a blank determination, the solution was made up as nearly as possible to the composition of the solution of the salt; *viz.*, twenty cc. ammonia, twenty-five cc. sulphuric acid (1–4) and water to the same volume.

In giving the results of our experiments, it seems unnecessary

to give all the figures as they comprise several hundred in number, extending over a period of six months. Only those illustrating the facts of interest are therefore annexed.

The most curious result obtained was in an effort to get the greatest possible reduction of the solution by repassing it through the reductor, heating it nearly to boiling after each passage. In the third passage, the solution instead of coming through green in color, was almost colorless and the green oxide of molybdenum was found deposited on the zinc in the reductor. In another attempt to reduce the molybdic acid by treating the solution in a flask with zinc in a current of hydrogen at a boiling temperature, redissolving the excess of zinc by sulphuric acid admitted through a funnel tube, allowing the solution to cool in the current of hydrogen after diluting by means of the funnel tube with boiled distilled water and titrating in the flask, the following results were obtained:

Weight of phosphomolybdate	0.08784 grams.
Volume of permanganate required	24.9 cc.–24.9 cc.
Molybdic acid on Mo_2O_3 theory.....	84.86 per cent.
" " " $Mo_{24}O_{37}$ "	87.28 "
" " " $Mo_{12}O_{19}$ "	89.85 "
" " " Mo by grav. det	91.96 "

showing that the reduction was not even to $Mo_{12}O_{19}$.

A series of determinations was made to test the best rate of speed for passing the solution through the reductor, and for a column of zinc from two hundred to two hundred and fifty mm. no appreciable difference was noticed between a speed of two minutes and one of ten minutes for the passage of a solution made up in the usual way, except that it was necessary to follow the solution of phosphomolybdate by dilute sulphuric acid when the rate of speed was very slow to avoid leaving some molybdenum trioxide in the zinc. This precaution was finally made a part of every determination and the beaker which contained the solution to be reduced, was washed down with a hot solution of sulphuric acid (ten cc. of sulphuric acid (1–4) diluted to 100 cc.) and the operation was completed by washing with water. A speed of about two minutes was finally adopted with a hot solution. It was also found advisable to pour fifteen cc.

of sulphuric acid (1–4) into the titrating flask, before attaching it to the reductor.

The following results will illustrate the effect of dilution:

Weight of phosphomolybdate.	Volume of solutions in cc.	Permanganate required in cc.	MoO_3 by $Mo_{24}O_{37}$ theory. Per cent.
0.03095	175	9.0	88.83
0.03095	175	0.2	90.80
0.06190	175	18.35	90.55
0.06190	175	18.40	90.80
0.15475	175	46.40	91.59
0.15475	175	46.35	91.49
0.03589	500	10.1	85.76
0.14356	500	42.6	90.64
0.07178	500	20.9	88.94
0.14356	250	43.1	91.71
0.07178	250	21.0	89.36
0.14356	125	43.05	91.60
0.07178	125	21.5	91.49
0.09720	50	29.1	91.45
0.09720	50	29.05	91.29
0.09720	75	29.2	91.77
0.09720	75	29.1	91.45

These results all point to the fact that it is desirable to have the solution sufficiently concentrated, and a volume of 100 cc. was finally adopted as being most satisfactory for general use and for weights of phosphomolybdate up to two-tenths gram. With greater amounts of phosphomolybdate it is necessary to increase not only the volume of the solution but also the amount of sulphuric acid in order to prevent the reprecipitation of the ammonium phosphomolybdate in the acid solution.

Many variations in the manipulation were tried, such as passing a small volume of dilute sulphuric acid through the reductor, following this with the solution of phosphomolybdate without allowing any air to pass in and completing the operation by washing with dilute sulphuric acid and water which had been boiled to expel the air, but no higher results were obtained, and we concluded that the reduction was practically to $Mo_{24}O_{37}$ and not to Mo_9O_8.

Secondly, to determine whether the methods in ordinary use would give results agreeing with these, it was determined to

send portions of this sample to the members of the sub-committee and also to Prof. Noyes and Mr. Doolittle. These samples were sent in the weighing tubes with the request that the tube be dried at 100° C. for about an hour and cooled in a desiccator. Then that about one gram be weighed out by difference, dissolved in ammonia, diluted to 250 cc. and portions of twenty-five cc. each measured off, acidulated and titrated in the usual manner; then that the results be returned in the following way; weight of phosphomolybdate used for the reduction, corrected volume of permanganate required for the oxidation, value of permanganate in iron. These returns were then calculated, giving the following interesting results.

MoO_3 IN SAMPLE 10 PHOSPHOMOLYBDATE.

	Mo_2O_3 theory. Per cent.	$Mo_{24}O_{37}$ theory. Per cent.	$Mo_{12}O_{19}$ theory. Per cent.	Gravimetric. Per cent.
Blair	88.91	91.45	94.14	91.96
Dudley	88.61	91.11	93.83	
Drown	88.68	91.21	93.90	
Shimer	88.22	90.74	93.41	
Doolittle (Job)	90.47	93.05	95.80	
Noyes	89.95	92.52	95.25	
Average		91.68		91.96

May we not conclude from these results—

First, that the ratio of phosphorus to molybdic acid is 1.794?

Second, that the value of molydic acid as compared with iron is 0.88163 according to the theory of reduction of the molybdic acid to $Mo_{24}O_{37}$?

MOLYBDATE SOLUTION.

In the course of this investigation, our attention was naturally called to the stability of molybdate solutions and the composition of the yellow precipitate which forms sooner or later in nearly all these solutions.

This precipitate carefully collected, washed with dilute nitric acid and then with cold water and dried over sulphuric acid was bright orange colored and contained by analysis,

Molybdic acid	90.43
Water at 250° C.	9.61
Phosphoric acid	None
Ammonia	Traces

When heated the precipitate became white and was in fact molybdic anhydride. As ammonium phosphomolybdate is much less soluble in dilute nitric acid containing ammonium nitrate than in dilute nitric acid alone, we considered it possible that the excess of ammonium nitrate might be the cause of the instability of these solutions and an experiment showed this to be the case. We found that the solution prepared according to the following formula remained practically unaltered for several months and gave exactly the same results as a fresh solution when used for the determination of phosphorus in steel. The following is the formula and method of preparation:

One hundred grams of molybdic anhydride was thoroughly mixed with 400 cc. of cold distilled water and eighty cc. of ammonia (0.91 sp. gr.) was added. This completely dissolved the molybdic acid. The solution, after filtering to remove any silica or dirt, was poured into a mixture of 300 cc. nitric acid (1.42 sp. gr.) and 700 cc. water. The solution did not become very warm and there was very little tendency on the part of the molybdic acid to separate out during the mixing.

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THE FERRATES.[1]

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"WHO has first seen ferric acid?" This question forms the pertinent title of a controversial article in the *J. Prakt. Chem.*, **32,** 448, and it is there stated that G. E. Stahl discovered that when saltpeter is ignited with iron and the mass is added to water, the caustic alkali resulting from the decomposition of the saltpeter holds a part of the iron in solution and produces an amethyst or purple color. He also stated that if dilute solutions of iron in nitric acid are poured in successive small portions into a strong solution of caustic potash the iron is dissolved on shaking, with a blood-red color.

While verifying the accuracy of the former I have not been able to reproduce the latter of these reactions. On its face it

[1] Read at the Brooklyn meeting.

looks so improbable that it must be believed that the statement is erroneous. Probably the nitric acid that Stahl used contained sufficient hydrochloric acid to make the reaction possible. Be this as it may, certain it is that the direction given by Stahl for making potassium ferrate in the dry way, through the ignition of saltpeter with iron, is sufficiently clear to be successfully followed, so that he is undoubtedly entitled to the credit of being the discoverer of ferric acid.

As recently as in Muir & Morley's edition of Watt's Dictionary of Chemistry, London, 1889, page 547, it is stated that "Stahl noticed in 1702 that a violet solution is obtained by fusing iron with saltpeter and washing with water or by adding a solution of iron in HNO_3 to conc. KOH aq.," which shows that these two editors had nowhere found a correction of the erroneous statement of Stahl, nor has a correction been published by any one until now.

In 1802 potassium ferrate was rediscovered by Ekeberg, while fusing gadolinite, which is a silicate of yttrium, beryllium, and iron, with caustic potash. In this experiment the ferric oxide, of which the gadolinite contains sixteen per cent., was oxidized in the presence of caustic potash so as to form potassium ferrate. However, neither Stahl nor Ekeberg examined the character of the iron compound which resulted from the reaction with the caustic potash, either added or produced in the process, and which gave rise to the claret color observed.

When Fremy undertook an investigation of those compounds of the metallic oxides, in which the latter play the part of acid metallic anhydrides, he very soon rediscovered the solution of ferric oxide in caustic potash. In this solution he found that the oxide did not exist as ordinary ferric oxide, Fe_2O_3, but that it contained more oxygen than the latter, the quantity of oxygen contained corresponding roughly, or as closely as it was possible to analytically determine the constitution of an impure and somewhat variable body, such as barium ferrate, to the formula FeO_3, a result which has since been confirmed by J. Denham Smith and H. Rose.

The accounts of Fremy's work were published from time to time in a number of scientific periodicals, commencing with

January, 1841, when he states that the compound of oxide of iron and potash which is soluble in water corresponds in composition to the manganates, and in 1842 the new compound was called by him ferric acid, though the name had already been suggested by J. Denham Smith in Phil. Mag. Ser. [3], **19,** 302.

Besides producing potassium ferrate by the methods of Stahl and Ekeberg, which were unknown to him, Fremy also obtained it by electrolyzing caustic potash with an anode of cast iron and also by introducing chlorine into a solution of caustic potash containing ferric hydroxide in suspension. In addition he produced this salt by heating iron with potassium dioxide.

In attempting to produce sodium ferrate by such processes as Stahl and Ekeberg had used to produce potassium ferrate he failed. Not only did Fremy fail in his attempts to produce sodium ferrate in the dry way, but there is not to be found in the literature of the subject any account of anybody else who has succeeded in doing so or who has ever suggested the possibility of its being accomplished. In fact the statement occurs in chemical literature that sodium ferrate cannot be made except in the wet way. Thus in Wurtz' Dictionnaire de Chimie, Volume 1, Part 2, page 1413, the following is found: "Sodium ferrate is soluble in water and cannot be prepared except in the wet way."

Bloxam prepared a solution of sodium ferrate by adding bromine to a strong solution of caustic soda containing ferric hydroxide in suspension. This I have found a very quick and convenient method of producing a small quantity of a solution of sodium ferrate. I have also several times made the attempt to produce sodium ferrate by the addition of iodine to a solution of caustic soda holding ferric hydroxide in suspension, but no sodium ferrate was formed.

Bloxam also found that a solution of calcium ferrate may be produced by gently heating a solution of bleaching powder with a small portion of ferric chloride. On repeating this experiment I have found the process to be a very delicate one and that it often fails, although, if very carefully conducted a rose-red solution of calcium ferrate is formed. I thought that perhaps by the addition of lime to the bleaching powder solution the reac-

tion might take place more expeditiously. Such, however, was not the case, as a solution of calcium ferrate could never be produced when lime was first added to the bleaching-powder solution containing a small portion of ferric hydroxide in suspension.

It was first stated by Fremy and it has subsequently been repeated in the text-books that calcium ferrate, like barium ferrate, is insoluble in water. The experiment of Bloxam above referred to shows that this statement is not correct.

On preparing a solution of sodium or potassium ferrate allowing it to stand, it sometimes changes color from red to green. J. Denham Smith believed this green solution to be caused by some new iron compound, but Heinrich Rose showed that it was derived from manganese. The ferrate solution prepared contained a manganate. On standing, the ferrate decomposed while the manganate remained unchanged until at last only manganate remained, when the solution turned green. I have repeatedly verified the correctness of Rose's explanation.

In undertaking a course of investigation of the properties of ferric acid the following interesting problems presented themselves:

1. Production of sodium ferrate in the dry way.
2. Production of iron dioxide.
3. Decomposition of barium ferrate by metathesis so as to obtain in this way a normal ferrate containing no free alkaline hydroxide.
4. Determination of the constitution of the thioferrates.

1. PRODUCTION OF SODIUM FERRATE IN THE DRY WAY.

In the attempts to produce sodium ferrate in the dry way, ferric oxide, both dry and hydrated, was calcined with caustic soda, sodium carbonate, sodium nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate, but all in vain. The substitution of sodium chlorate for a part or all of the sodium nitrate was also tried but with no change in the result. Sodium dioxide was then tried, but at first without success. It was however observed that when the fused mass from this last experiment had been allowed to cool, on subsequent addition of water it became highly heated, and

it was suspected that while sodium ferrate had been produced by the reaction, that it was at the same time decomposed by the heat, resulting from the addition of the water, and it was believed that if this rise in temperature could be obviated the decomposition of the ferrate might be prevented. This theory was acted on and the mass resulting from the fusion of the ferric oxide and the sodium dioxide was treated with ice, and though some rise in temperature still followed it was much less than before, and sodium ferrate was obtained in solution. Thus the first problem had been successfully solved and sodium ferrate was for the first time produced in the dry way. There are two probable reasons why Fremy failed. In the first place, when using sodium nitrate this was to a great extent decomposed by the heat leaving behind sodium nitrite which is stable at high temperatures, and which, when the mass was dissolved in water served as a reducing agent, reducing the iron trioxide to the ordinary ferric oxide, while the nitrite itself, by oxidation, became converted into nitrate. When using caustic soda the cause of the failure was probably the heating of the mass on the addition of water, which heating has already been referred to.

II. ATTEMPTED PRODUCTION OF IRON DIOXIDE.

The production of iron dioxide was of course the most important of the problems. The hope of accomplishing this result was the inciting cause of the investigation and a great number of experiments were conducted with this end in view.

As it is well known that chromium dioxide can be readily obtained by adding a solution of a chromic or chromous salt to a chromate it would seem at first sight that, having the iron monoxide and the trioxide, the iron dioxide might be easily prepared by an analogous reaction to the one above mentioned.

To produce a precipitate of iron dioxide from a solution of sodium ferrate, which is highly alkaline, the solution of the iron salt added would have to be alkaline. Such a solution may be made in many ways, such as by the addition of tartaric acid, citric acid, or glycerol, to a solution of a ferric salt and then adding a caustic alkali in excess, but in each case the organic solvent was oxidized before any precipitate was formed and so this method had to be abandoned.

The addition of barium ferrate to solutions of ferric chloride, both normal and basic, was tried with apparently good prospects of success as the barium went into solution as chloride, but at the same time oxygen and also chlorine were given off, so that the precipitate ultimately obtained consisted merely of ordinary ferric hydroxide. For the purpose of this experiment, the barium ferrate was just as good as normal sodium ferrate could this latter be produced; the barium ferrate decomposed the ferric chloride perfectly, so that if iron dioxide is capable of production, here the conditions of success seemed to be the best and yet the result of the reaction was only ordinary ferric oxide. Hence, it is quite certain that if iron dioxide can be made at all, it is a compound of such exceeding instability as to have decomposed as fast as formed.

III. THE REACTIONS OF BARIUM FERRATE.

Of the ferrates the most stable, the one that can be prepared in the purest state and the most definite in composition is barium ferrate, $BaFeO_4.H_2O$, this formula having been determined by Fremy and H. Rose. Before barium ferrate has been allowed to dry it is decomposed by all the soluble acids, including carbonic acid. After it has once been allowed to dry in a desiccator it is not so easily decomposed, at least completely. If barium ferrate, which has not been allowed to dry, be suspended in water through which carbon dioxide is passed, it will be completely decomposed with the formation of barium carbonate and ferric hydroxide, oxgen being set free. From this decomposition it might reasonably be expected that iron dioxide would be formed just as manganese dioxide is formed on passing carbon dioxide through water containing barium manganate in suspension, but such is not the case. This experiment would also seem to indicate that neither a compound of iron, corresponding to a permanganate nor a compound corresponding to a bichromate exists. The result of passing carbon dioxide through water containing barium ferrate in suspension, with the object of obtaining new iron salts therefore carries with it two disappointments.

When barium ferrate has been thoroughly dried in a desicca-

tor it is readily attacked by acids, but complete decomposition is not readily effected in the cold even with dilute sulphuric acid, oxalic acid, formic or acetic acids. Hydrochloric acid decomposes it completely with the greatest readiness, chlorine being always set free. If barium chromate be digested with a solution of sodium ferrate, barium ferrate is formed and the solution changes color from red to yellow, due to the sodium chromate which has been formed. The reverse reaction never takes place. Thus, if barium ferrate is digested with a cold solution of an alkaline carbonate, sulphate or triphosphate, an alkaline ferrate is never formed, the solution remaining colorless. An alkaline sulphate will decompose barium ferrate that has not been dried with the formation of barium sulphate and ferric hydroxide, oxygen being set free. It thus appears that barium ferrate is one of the most insoluble salts known. It is strange that in none of the publications up to this time has the behavior of barium ferrate to neutral salts been referred to.

IV. THIOFERRATES.

Fremy states that on passing hydrogen sulphide through a solution of sodium ferrate a solution is obtained of a beautiful emerald color. He supposed that the sodium ferrate was converted into sodium thioferrate. On passing hydrogen sulphide through a solution of sodium ferrate I sometimes obtained the green solution described by Fremy and at other times not. Investigating the matter, I found that the green solution was obtained only when the original solution contained manganese. It appears then that on passing hydrogen sulphide through a ferrate solution containing a manganate the ferrate is reduced by the hydrogen sulphide, leaving the green manganate solution behind. If, on the other hand, the ferrate solution contains no manganese, on passing hydrogen sulphide through it, the red color disappears and a solution is obtained having a greenish yellow tinge, such as is obtained by digesting precipitated iron sulphide in a solution of an alkaline polysulphide, the greater part of the iron being precipitated as black sulphide. The supposed thioferrates must therefore be considered as mythical.

The only use so far suggested for the ferrates, is the produc-

tion of oxygen described in British Patent, No. 85, Jan. 10, 1886, to Brooman, a communication by Maréchal and Tessie du Motay, in which it is stated that potassium, sodium, and barium ferrate may be decomposed by a current of steam and subsequently reformed by the action of a current of air at high temperature.

Whether the ferrates resemble the chromates or manganates more is difficult to say. If a salt could be produced corresponding, either to the bichromates or the permanganates the question would of course be immediately decided. The extreme insolubility of barium ferrate, together with the solubility of calcium ferrate, as well as the instability of the dioxide, if it does exist, brings the ferrates closer to the chromates than the manganates. On the other hand the soluble ferrates can only exist in alkaline solutions, and in this respect they resemble the manganates. In their oxidizing power the ferrates still more closely resemble the manganates. It has already been stated that a ferrate will oxidize nitrites, tartrates and glycerol. The soluble ferrates are also decolorized or reduced by oxalates, alcohol, ether, ammonia, urea, and other soluble organic bodies with very few exceptions, such as, and notably, the acetates. They are decomposed also by some insoluble organic bodies, such as paper and insoluble carbohydrates, but most insoluble organic bodies, such as the paraffines and benzene, decompose them but very slowly.

To perform all the experiments on ferrates above referred to, sodium and potassium ferrate had often to be prepared. Of all the methods of making these salts the easiest is to pass chlorine through a strong solution of sodium hydoxide, containing ferric hydroxide in suspension. At one time I produced sodium ferrate on a scale never before attempted. Three kilos of sodium hydrate were dissolved in enough water to form ten liters of solution. To the solution were added 150 grams of ferric chloride, and the mixture stirred for a long time until the ferric hydroxide formed was all finely divided and evenly distributed throughout the solution. Through the mixture chlorine gas was then passed from a cylinder of liquid chlorine which had kindly been presented by my friend Dr. Rudolph Knietsch, one of the leading chemists of the Badische Anilin und Soda Fabrik of Ludwigs-

hafen, Germany. The operation was carried on very successfully, the chlorine gas passing through with great regularity, and in this manner a quantity of stock solution was prepared sufficient for all subsequent experiments.

It may here be stated that whenever an experiment is described above it has been actually tried for the purpose of making sure that the reaction indicated actually takes place.

The following is a summary of the errors which occur in the literature of ferric acid:

1. The direction for making potassium ferrate by adding iron nitrates to caustic potash, by Stahl.

2. The statement that on standing a solution of potassium ferrate changes color and turns green, made by J. Denham Smith.

3. The statement that calcium ferrate is insoluble in water, made by Fremy.

4. The direction for making thioferrates by passing hydrogen sulphide through a solution of a ferrate, by Fremy.

5. The allegation that sodium ferrate cannot be made except in the wet way, made by Wurtz.

Of these, the second error was corrected by H. Rose and the third by Bloxam, the other three having now for the first time been brought to light.

In the annexed bibliography are included only original articles, and when articles have been reprinted in different periodicals, only the first has been given. The full titles of the articles referred to have been perused, so that it is certain that they exist and relate to the subject-matter indicated.

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[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA SUGAR EXPERIMENT STATION AND SUGAR SCHOOL.]

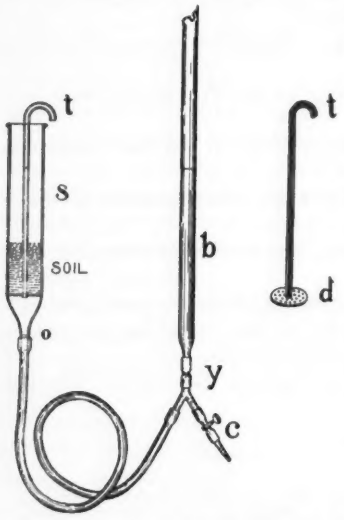
A SIMPLE AND CONVENIENT APPARATUS FOR ESTIMATING THE WATER-HOLDING POWER OF SOILS.

BY J. L. BEESON.

Received June 3, 1895.

TO a fifty or 100 cc. plain burette is connected a glass Y tube by means of a piece of rubber tubing. To one of the forks is attached a bit of rubber tubing carrying a pinch-cock, and the other fork is connected with a small Stutzer extraction tube, having a zero mark scratched on its neck, by means of a stout piece of rubber tubing about two and one-half feet long. The apparatus is fastened in the clamp of an ordinary clamp-stand. A metallic disk, which will about fit the larger tube, is perforated with many small holes, the center with a larger hole that will admit the end of a piece of glass tubing, which is made firm by

fusing into the glass by means of a burner or blast lamp. The upper end of the tube, d t, is bent over so that the soil will not fall into it while filling the larger tube. Disks of filter-paper, of convenient size, are perforated with a cork borer, and one of these is slipped over the glass tube down against the perforated disk, and held down by means of a rubber washer cut from a piece of small rubber tubing. The edges of the paper are folded under the disk so as to make it fit the tube well, and the whole slipped down to the bottom of the large tube. The apparatus, which is now ready for use, is very simple, and much more rapid and convenient, it is believed, than the one devised by Mr. Feulling as described in Dr. Wiley's book on soil analysis. The apparatus is filled with water, the burette raised so as to cover the disk and filter-paper and then lowered. The excess of water will now run out of the filter-paper so that the reading will become constant within five minutes. Then by means of the pinch-cock c water is slowly drawn off until it stands at the zero mark on the neck of the tube o, and at zero on the burette. From twenty-five to fifty grams of soil, according to the water-holding power of the sample, is added to the large tube S, which is gently tapped until the soil is level. The burette is raised and the water gently forced into the soil from below until it forms a level above the soil. From the height of the column of water in the air-tube t the amount of pressure may be seen. The burette is then lowered and the water runs out of the soil by gravity alone, since the space below the disk is supplied with air through the tube t. When there is no more rise of water in the tube, which requires about fifteen to



twenty minutes, the burette is raised until the water stands at the zero mark o in the tube, when the number of cc. of water absorbed by the soil is read on the burette. The whole time for an analysis need not exceed thirty or forty minutes. The pinch-cock on the Y tube is most convenient in bringing the water to the zero marks on the tube and burette before adding the soil. The apparatus may be obtained of Kæhler and Martini, Berlin.

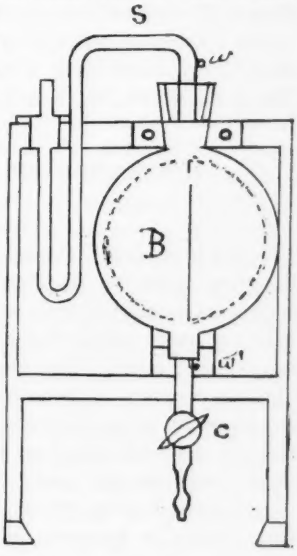
A MODIFICATION OF HINMAN'S EXPLOSION PIPETTE.

By Augustus H. Gill.

Received August 7, 1895.

THIS pipette was devised to permit the use of all the residue, sixty cc., remaining after an illuminating gas had been analyzed by the Hempel apparatus, in mixing with oxygen for explosion.

It consists of a bulb, B, eleven to twelve cm. in diameter, of about 250 cc. capacity, with walls at least twelve mm. thick, provided with two tubulatures; at the bottom a stop-cock, C, is ground in for regulating the flow of mercury; to the top one is fitted the capillary stem, S, which must be very carefully ground in. These joints are first vaselined, care being taken that none gets inside the apparatus, and cemented in with a sealing wax having nearly the same coefficient of expansion as glass. Metal clamps hold the bulb upon the stand, similar to that for the simple pipette,[1] the weight of the bulb being sufficient to keep it in the lower one; the upper one is provided with screws to hold the neck of the bulb. To render the stem-joint more nearly tight the upper tubulure is made with a mercury seal an inch deep. As thus constructed, the apparatus is



[1] Gill, *Am. Chem. J.*, 14, 231.

absolutely tight at all pressures to which it is likely to be subjected.

Both spark wires were originally fused through the capillary stem, but from the oxides of nitrogen and carbon dioxide formed during the explosions an electrical connection was established sometimes between them and no spark was visible upon turning on the current. To obviate this, one fine spark wire, *w*, is fused through the capillary and the other, *w'*, a platinum wire one and a half mm. in diameter passes through a rubber fitting in the tube carrying the stop-cock up through the mercury to within two mm. of the other. A Mariotte bottle conveniently serves as a reservoir for the mercury and is connected with the pipette by quarter inch "pressure tubing."

It sometimes happens that no spark passes upon closing the circuit. This can be remedied by sucking water into the pipette and expelling it. Upon allowing it to stand all the moisture rises to the top and may be driven out.

The apparatus has been in use for four years, scores of explosions having been made with it. It may be obtained from the Ziegeler Electric Co., Franklin St., Boston.

ESTIMATION OF SULPHUR IN PYRITES.

By G. LUNGE.

Received June 4, 1895.

IN this Journal Mr. Gladding replies to my remarks on his previous paper on the estimation of sulphur in pyrites. His comments would certainly not give to any reader, who had not my own paper before his eyes, a fair idea of its purport. He states that I admit "that every modification proposed (by Gladding) is accurate in its nature, with one single exception." This conveniently passes over the fact that my "admission" had been saddled with the following addition, for which I had adduced ample experimental proof, "that not in a single case is Gladding's method more correct than mine, and that his modifications cannot be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever."

In one point, and that just relating to the principal novelty in Gladding's process, I declared him to be entirely *wrong; viz.*, in his denial of the fact that it is very easy, by a special kind of washing, to avoid leaving any sulphur in the ferric hydroxide. This point is even more decidedly misrepresented by Gladding (of course, unintentionally) than the others. He says that I "admit that students in my own laboratory have sometimes failed to get out all the sulphur, through imperfect washing." I must really complain of this way of quoting my paper against myself, seeing that I immediately followed up the above by the express statement that such failures occurred in *every* case through having washed in the usual way, instead of the special way prescribed by me for that object; and that the same men have succeeded in every case after their attention had been drawn to this point. That beginners, like those I was speaking of, will make mistakes in most other analytical methods as well, until their attention is drawn to their having neglected some essential precautions, is too patent to be dwelled upon. Nor is it my business to find out why Mr. Gladding and his assistants have failed in a process which succeeds in the hands of *all* beginners in my laboratory, and which is practised by hundreds of chemists, none of whom have ever found any fault with it.

After such an involuntary "admission" of imperfect manipulation on Mr. Gladding's part, it is not possible to take the accuracy of his further results for granted which are contradictory to mine, concerning the differences between our two methods. I repeat that I have afforded in my paper, by a large number of comparative assays, complete proof that (except when the washing was intentionally interrupted before completion) absolutely the same results are obtained by both methods, mine, however, taking considerably less time than his. It seems to me perfectly unnecessary to repeat such proofs, since nothing new can possibly be brought out by it, and I must altogether decline to carry on further discussion with an opponent who treats my paper and work in the above-mentioned style, rewarding my studied fairness by construing it into all sorts of distorted "admissions," and not appreciating the perhaps exaggerated courtesy with which I had explained a decided error in his description of the

decomposing-mixture as being perhaps due to a clerical mistake.

Mr. Gladding seems to have felt that it was necessary to bring heavier metal against me than his own assertions, and he therefore quotes a private communication from Prof. Richards, of Harvard College. He does not mention anything of Prof. Richards having sanctioned the verbatim publication of the "private" communication. For my part, until the contrary is proved, I beg leave to doubt that Prof. Richards would *publicly* have used expressions accusing me of ignorance on a point "which has been known for a number of decades;" *viz.*, the occlusion of barium chloride on the sulphate. Before doing so, he would have looked not merely at my last paper, but also on those I had previously written on the estimation of sulphur in pyrites. He would then have found that I have made researches on this subject for the last fifteen years, and that in my communications the previous work of Fresenius, concerning the difficulty of removing the barium chloride from the sulphate, is referred to as common knowledge. He would then not have misunderstood my last paper as denying that patent fact, which he has so thoroughly investigated in a paper published subsequently to mine. He would have acknowledged that I could not have meant anything else than claiming for my special process the greatest possible approach to truth, which would *not* be attained by preventing all and every occlusion of barium chloride, seeing that the solubility of the barium sulphate in the acid liquid must cause an error in the opposite direction. I am quite sure that Prof. Richards, like every other chemist, is aware of the fact that not one of our analytical separations is mathematically perfect, and that the best analytical methods are those in which unavoidable, but opposite errors are as nearly as possible balanced, and which thus gives a closer approximation to the truth than methods in which one of these errors is eliminated, but the compensating error in the opposite direction is allowed to remain. I have never claimed that the precipitate of barium sulphate obtained according to my method was absolutely devoid of barium chloride, no more than, in the opposite direction, that no barium sulphate whatever remained dissolved in the acid liquor; my claim has been that my method, by compensation of unavoidable errors, gives *correct*

results. I need not, however, comment any further upon Prof. Richard's private letter to Mr. Gladding, since everything of importance in this controversy is settled by an authority which Prof. Richards will certainly approve of; *viz.*, a passage in his own paper in the *Zeitschrift für anorganische Chemie*, *1895*, **8**, 418, which I translate verbatim:

"Moreover the observation is of interest, that the error caused by occlusion ordinarily just about compensates that caused by the solubility of the sulphate, so that the final corrected result is almost the same as the real weight. The average of the uncorrected results is 0.3215 in lieu of 0.3214 gram."

This, I think, disposes of the aid which Mr. Gladding has solicited from Prof. Richards in his attack upon me.

ZURICH, MAY 23, 1895.

THE PERIODIDES.[1]

BY ALBERT B. PRESCOTT.

Received August 12, 1895.

THE periodides are remarkable as products of extreme additive combination, along with clearly cut crystalline form, distinct physical constants, and instances of rare optical power. They are easily reduced to normal iodides, containing for every atom of iodine firmly bound, one or more iodine atoms loosely bound; therefore they are often and not improperly termed superiodides. Professor Geuther used for them the term polyiodide, perhaps by reason of his view that all their iodine atoms are of equal valence in the molecule.[2] Jörgenson designated them together as superiodides, though including within their structural type certain double polyiodides not understood to contain additive iodine.[3] If these compounds contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked. The one iodine atom that is directly united to the nitrogen or other

[1] Read at the meeting of the American Association for the Advancement of Science, Springfield, Aug. 30, 1895.

[2] A. Geuther, *1887*: *Ann. Chem.* (Liebig), **240**, 82.

[3] M. Jörgenson, *1869*: *Ber. d. chem. Ges.*, **2**, 465.

base-forming element, by virtue of this union, enables a number of other iodine atoms (say from two to eight) to unite with each other together with itself in an iodine group, capable of forming multiples in polybasal molecules. To this view we are led, possibly misled, by the course of theory. In this relation the molecular weight of free iodine is of interest, and has been studied with care, not only in the vapor[1] but in solutions[2] and in the crystals[3] themselves. The relation to the elemental molecules gives to the periodides an interest greater than that of the mixed superhalides, such as iodoperchlorides and iodoperbromides of bases inorganic and organic. The supersulphides, however, present a corresponding instance of additive combination with a single element, as understood. The organic supersulphides[4] are not so ready of formation or so stable as the organic superiodides, though the reverse seems to be true of the corresponding inorganic super compounds. In its elemental states sulphur surpasses iodine in its unusual capacity for polyatomic molecules. And this comparison holds for the hydrides, as hydrogen pentasulphide was reported in 1888[5], while hydrogen diiodide, though holding a name in the earlier handbooks[6] is no longer accounted a chemical individual.[7] Again, the superoxides of organic acid radicals were compared with superiodides by Brodie.[8]

To obtain a general survey of the principal known periodides, they may be provisionally classified, chiefly with respect to their bases, as follows:

1. The periodides of potassium and of mercury. Any double metallic polyiodides containing additive iodine and without other acid.

[1] V. Meyer, *1880*: *Ber. d. chem. Ges.*, **13**, 1010; Neumann, *1880*: *Ber. d. chem. Ges.*, **13**, 1050.

[2] M. Loeb, *1888*: *J. Chem. Soc.*, **53**, 805; Paterno and Nasini, *1888*: *Ber. d. chem. Ges.*, **21**, 2153; Krüss and Thiele, 1894; *Ztschr. anorgan. Chem.*, **7**, 52; John Conroy, 1874: *Proc. Roy. Soc.*, **25**, 46.

[3] John Conroy, *1876*: *Proc. Roy. Soc.*, **25**, 51; Compare Geuther, *1887*, *Ann. Chem.* (Liebig), **240**, 85.

[4] Palm, 1863: *Phar. Ztschr. Russ.*, **2**, 337, 361, 385; A. W. Hofmann, *1868*: *Ber. d. chem. Ges.*, **1**, 81; E. Schmidt, 1876: *Ann. Chem.* (Liebig), **180**, 287; A. W. Hofmann, again in 1877, *Ber. d. chem. Ges.*, **10**, 1087.

[5] Rebs: *Ann. Chem.* (Liebig), **246**, 356.

[6] Gmelin's Handbook, **2**, 261, *1849*, from Baup, *J. Pharm.*, **9**, 40.

[7] Gmelin-Kraut's Handbuch, I, **2**, 310, *1872*. [8] *J. Chem. Soc.*, **2**, 281, *1876*.

2. Periodides of ammonium. Periodides of arsonium[1] and of stibonium if they have been obtained. Periodides of the metallic derivatives of ammonium. The same of metallic derivatives of arsonium and of stibonium, if they have been obtained.

3. The periodides of organic bases. They are mostly of the quaternary, and the tertiary[2] bases, of the nitrogen-base family, including bases with oxygen and without it. Phosphonium,[3] arsonium,[4] and probably stibonium[5] periodides are known. And, of another type, that of perhalide of a bare amine base, such as $(R_3N)I_2.I$, at least triethyl phosphine periodide[6] and pyridine periodide[7] have been reported. Also a perhalide taken as pyridine dibromide hydrobromide.[8] The nitrogen-base periodides belong in two categories, (1) those of the alkylammonium bases, and (2) those of pyridine and its derivatives. Polyiodides of the vegetable alkaloids belong in the latter division, except the caffeine and theobromine polyiodides.

4. The periodide of iodonium, the organic iodine base obtained by Victor Meyer last year.[9] The normal iodide of iodonium is of structural interest to polyiodides generally.

5. Aromatic sulphon periodides, as found by Kastle and Hill last year.[10]

6. Acid polyiodides, more or less complex, and double base polyiodides, inorganic and organic, including those in which the iodine is not in additive combination, that is, *not* yielding a distinct part of the iodine to reducing agents with a good end reaction.

[1] Phosphonium *normal* iodide; Labillardiére and Gay Lussac: *Ann. chim. phys.* [2], **6**, 304; A. W. Hofmann, *1887*; *Ann. Chem.* (Liebig), **103**, 355; 1873: *Ber. d. chem. Ges.*, **6**, 286. Inflames by contact with iodine.

[2] In Geuther's table, in 1887, of the periodides then known, the only periodides of tertiary bases destitute of oxygen, which appear are a pyridine hydrogen pentiodide, and a quinoline hydrogen tetriodide, both by Dafert (Geuther: *Ann. Chem.* (Liebig), **240**, 74). In reporting upon these, in 1883, Dafert says: "Nach den bis jetzt bekannten Thatsachen schientes, dass nur tertiäre und Ammoniumbasen Periodide bilden" (*Monatsh. Chem.*, **4**, 510.)

[3] Tetraethylphosphonium triiodide, Jörgensen, *Ann. Chem.* (Liebig), **240**, 74.

[4] Tetraalkylarsonium triiodides, Cahours, *1860*: *Ann. Chem.* (Liebig), **116**, 346; *1862*: *Ibid*, **122**, 215.

[5] Jörgenson, *1869*: *Ber. d. chem. Ges*, **2**, 463.

[6] Masson and Kirkland, *1889*: *J. Chem. Soc.*, **55**, 139.

[7] Mr. Trowbridge and the author in another paper of this date.

[8] Grimaux, *1882*: *Compt. rend.*, **95**, 87; *Bull. Soc. Chim.*, **38**, 127.

[9] *Ber. d. chem. Ges.*, **27**, 1594, *1894*.

[10] *Am. Chem. J.*, **16**, 116. A sulphur periodide of another order is that obtained in amorphous condition by Jörgensen, *1869*: *Ber. d. chem. Ges.*, **2**, 464.

Geuther's classification into triiodides, pentaiodides, heptaiodides, and enneaiodides, all with one atom of iodine firmly bound,[1] was of service in his own study of structural features. But Geuther admitted a category of sesqui-, di-, tetra-, and hexaiodides. There is surely a prevailing proportion of *even* numbers of *additive* iodine atoms, making *odd* numbers of *total* atoms of iodine, per "molecule" of the periodide. Generally this is an assumed "molecule" of monobasal proportions. That two or more monovalent groups of the ammonium type should enter into the formation of a periodide molecule, in some cases, is theoretically probable, to say the least, if periodides are individualized in molecules at all. The hypothesis of Jörgenson in 1869,[2] providing for both monammonium and diammonium types of periodides, is not an unreasonable one. Moreover, there is to be considered the probable occurrence of an iodine atom in the fourth position of the organic ammonium group, phosphonium group, etc., with whatever degree of firmness of binding may be determined for it in this position. Take it all in all, therefore, it seems to me that at present we know no law of even or uneven numbers of iodine atoms in superiodides, either to help or to hinder our interpretation of results. With evidence of molecular weight we may gain approach to such a law.

In division 6 of the classification above there are without doubt included certain strictly normal iodides. The iodomercurates as strongly marked double iodides, and the Herapathites as representative acid superiodides come in this division. An interest in the iodomercurates of the nitrogenous bases[3] has been but one among several causes contributing to my own interest in this subject at present. But I have not yet made such an inquiry into the action of deiodinizing agents upon the known double iodides as might reveal what superiodides there are among them. Some of the tabulations of the super-iodine in double inorganic polyiodides given by Geuther[4] seem to invite further inquiry. The acid periodides in many cases undenia-

1 *Ann. Chem.* (Liebig), **240**, 74, 80, *1894*.
2 *Ber. d. chem. Ges.*, **2**, 465, *1869*.
3 *Am. Chem. J.*, **14**, 607, 1892; **2**, 294, *1880*. *Pharm. Rund.*, **12**, 146.
4 *Ann. Chem.* (Liebig), **240**, 81.

bly contain additive iodine, but the question of their constitution, like that of mixed halides in general[1] is more complicated and is perhaps of less special significance, than that of the simple polyiodides.

With the exception, then, of the metallic, the iodonium and the sulphon periodides, the formation of superiodides is limited, so far as I have found, to compounds of the nitrogen family of elements.

The first periodide recognized, so far as I find record, may have been that of ammonium, termed by Berzelius the biniodide. After the discovery of iodine the first workers upon the alkaloids seem to have mistaken, in some instances, a produced periodide for a mixed excess of iodine to be taken up by more alkaloid in preparation of the hydriodides.[2] In 1839 Bouchardat,[3] a medical writer in Paris, recounts that, when dogs were being surreptitiously poisoned with strychnine in Paris, and an antidote was asked for, first Guibourt recommended powdered galls, and then Donné advised iodine tincture,[4] whereupon Bouchardat himself, approving the use of iodine, said they should use it in potassium iodide solution. He then set forth some interesting characters of the alkaloid periodides, comparing them with ammonium periodide, quoting for this the name from Berzelius mentioned above. De Vrij has said that Bouchardat anticipated Herapath in production of iodosulphates. A modest memoir of Donné, in connection with the Parisian interest just referred to, upon the use of iodine as an analytical reagent for vegetable bases, was referred for criticism to D'Arcet and Chevreul, who made quite an elaborate report[5] upon the action of free chlorine, bromine, and iodine, in intensive application, with admonition as to undue dependance upon any single analytical reactions. In 1846, in his summary of the distinguishing reactions of the more important

[1] The Chloriodides of Organic Bases, and Pyridine Chloriodide, Pictet and Krafft, *1892*: *Bull. Soc. Chim.* [3], **7**, 72.

[2] Pelletier and Caventou, 1819. *Ann. chim. phys.* [2] **10**, 142; *Ann. der Phys. Gilbert*, **63**, 306.

[3] Bouchardat, 1839: *Compt. rend.* **9**, 475; *L'Institut*, **7**, 358.

[4] Both apparently acting under the opinion, due to that little chemistry which has often brought all chemistry into disrepute, that a precipitant in a test-glass will serve as an antidote in the stomach.

[5] *Ann. chim. phys.* [2] **38**, 82.

alkaloids,[1] v. Planta-Richenau specifies for each a precipitation by free iodine. In 1854, shortly after A. W. Hofmann's famous elucidation of organic ammonium bases,[2] Weltzien contributed a full and careful description[3] of the tetramethyl and tetraethyl ammonium triiodides. In 1858 Müller added a good account[4] of quaternary mixed alkyl ammonium triiodides. In 1866 Wagner[5] proposed iodine precipitation and a method of treatment of the periodide precipitates for separation of alkaloids from extractive matters. And Tilden made a contribution in 1866.[6]

The masterly work of Jörgensen, beginning with his dissertation at Copenhagen in 1869, continuing for about nine years[7] in this field, and extending over nearly all relations of polyiodides in general, have had the respect of all chemists, while hardly yet fully assimilated.

In 1887 this subject was taken up by Professor A. Geuther, at Jena, who contributed[8] a good number of new periodides from his own laboratory, with a tabulation of all then obtained, and a vigorous and independent study of the features of structure. The crystallographic investigations were made by Prof. Lüdecke. Prof. Geuther died in 1889.

In 1869 Jörgensen[9] formulated his idea of the probable structure of "these compounds," taking iodine as trivalent, as follows:[10]

$R_4N.I : \begin{matrix} I \\ \vdots \\ I \end{matrix}$; $R_4N.I : \begin{matrix} I.I \\ \vdots \\ I.I \end{matrix}$; etc., for periodides of uneven numbers of iodine atoms.

$R_4N.I : \begin{matrix} I.I.I \\ \vdots \\ I.I.I \end{matrix} : I.NR_4$ for those of even iodine numbers.

And $R_4N.I : \begin{matrix} I \\ \vdots \\ I \end{matrix} : Hg$ for a typical iodomercurate. This simple

[1] Heidelberg dissertation, 1846. *Ann. Chem. Pharm.*, **74**, 245.

[2] *1850–51*: Phil. Trans. I. 93-131, 357-398.

[3] *Ann. Chem. Pharm.*, **91**, 33; **99**, 1.

[4] *Ann. Chem. Pharm.*, **108**, 1.

[5] *Ztschr. anal. Chem.*, **4**, 387.

[6] *J. Chem. Soc.*, **19**, 145, *1871*.

[7] *J. prakt. Chem.*, 1870-78, [2] **2**, 347, 433; **3**, 145, 328; **14**, 213, 356; **15**, 65, 418; **16**, 352. *Ber. d. chem. Ges.*, **2**, 460, *1869*.

[8] *Ann. Chem.* (Liebig), **240**, 66-91.

[9] *Ber. d. chem. Ges.*, **2**, 465, *1869*.

[10] The present writer gives R_4N as an expression for any organic base of nitrogen, instead of "Alk" used by Jörgensen.

conception is, of course, consistent with an iodine valence of five or of seven.

Geuther[1] drew from the optical studies of the color of iodine crystals by Conroy the indication that the molecular mass of the crystalline element is that of $(I_6)_n$. He made this generalization as to color of the periodides, that the tri and hepta iodides were red-brown to violet-blue, and the penta- and enneaiodides green to green-black, the higher iodine numbers giving the deeper shades.[2] He presents structural schemes of orders as follows:

For the triiodides, $(R_6I_6)I_{12} = 6(RI.I_2)$; for the haptaiodides, $(R_2I_2)I_{12} = 2(RI.I_6)$; for the pentaiodides, $(R_4I_4)I_{16} = 4(RI.I_4)$; and for the enneaiodides, $(R_2I_2)I_{16} = 2(RI.I_8)$.

In the laboratory of the writer the preparation of periodides of pyridine is in the hands of Mr. P. F. Trowbridge, and an account of some of these is communicated by both of us in another paper, while he continues the work for pyridine and quinoline. Some work on periodides of the more simple of the aliphatic bases is in other hands. In this subject a pyridine normal polybromide, namely a trimethylene bromide, obtained by Mr. R. F. Flinterman, is reported upon in a paper by him and myself. Therewith it is desired to continue studies of the limit of tertiary base addition to halogen alkyls which are secondary and tertiary. I submit also a note with the observations of several workers upon the preparation and properties of a few pyridine alkyl normal iodides, and Mr. S. H. Baer has some work in progress with me upon pyridine alkyl hydroxides.

ANN ARBOR, MICHIGAN.

AN IMPROVED GAS REGULATOR.

BY F. P. DUNNINGTON.

Received August 7, 1895.

SOME years ago I published[3] a description of a gas-regulator, which is now so modified as to make it less bulky and more reliable. Its arrangement may be understood by reference to the

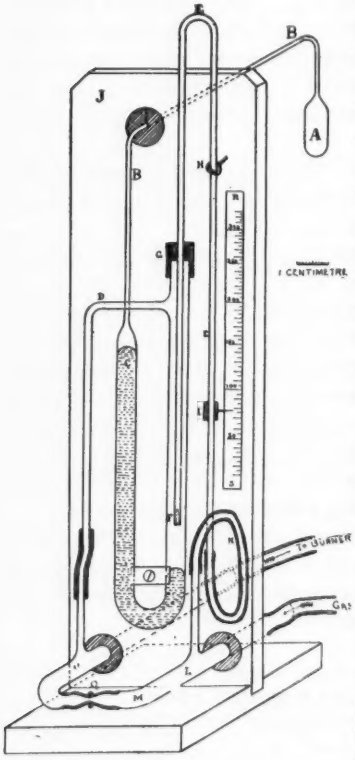
[1] *Ann. Chem.* (Liebig), 240, 85.

[2] This generalization, to which Prof. Geuther acknowledged reported exceptions, finds little support in the observations which Mr. Trowbridge and the writer have been able to make.

[3] *Am. Chem. J.*, 4, 2.

figure, with the accompanying scale the measure of the inner walls of the tubes may be ascertained, and other dimensions are drawn to two-thirds of this scale.

The tube B with stout walls, about forty cm. long is attached to the bulb A. Into the tube C, thirty-five cm. the small side tube D is fused. Unite C to B, and bend all as indicated. Into the tube L fuse the side tube and at M, bend at right-angles; similarly make the tube O. These latter are passed through corks, set in the upright board J. B also is passed through this board, which then serves to screen the apparatus from the heat of the bath, and C is firmly fastened to it.



The light tube E, fifty cm. long terminates at F with a slit, made by blowing a hole through its side and then drawing it out. This slides through a joint at G, made with two sections of rubber tubing, and also through a screw-eye at H. Upon E slides a bit of rubber tubing I, which is compressed by a wire around it, the end of which serves as an index. E is connected to L by fifteen cm. of light one-eighth rubber tubing, D is connected with O, and L is joined to O by a rubber tube pinched by a screw clamp at Q. A piece of card-board, RS, is pasted to the board. By warming and cooling the tube C is filled with mercury, as indicated. To graduate the apparatus, connect L with gas supply and O with a burner, pinch the tube at N, open Q sufficiently

to maintain a small flame, relieve N and push down E until the flow of gas through F just ceases; then slide the index I almost to the lower end of E, and upon the paper mark the point corresponding to the temperature of the bulb A. Place bulb A and a thermometer in a water-bath, with the burner beneath, and raise E. When the temperature of the bulb A is, say 50° C, lower E until the flow of gas through F just ceases, and make a mark on the scale for 50°, similarly fill out this scale to 100° C., and for higher temperatures employ an air-bath, or preferably a paraffin bath.

In using the apparatus, E is lowered until the gas through F is just cut off and the index is moved up or down the tube until it points to the figure marking the temperature of the atmosphere in which A is exposed. Having fixed the index, the tube E is raised until the index marks the temperature at which it is desired to maintain the bulb.

This adjustment of the index, whenever the regulator is used, eliminates the effect of the thermometer and barometric pressure upon the volume of air confined in A, B and C, and so corrects a defect existing in most instruments of this kind.

UNIVERSITY OF VIRGINIA.

INSPECTION OF COTTON FOR USE IN THE MANUFACTURE OF GUNCOTTON.[1]

BY CHARLES E. MUNROE.

Received August 2, 1895.

WHEN converting cotton into guncotton by immersion in mixed acids, as practiced in the Abel process, it is essential that the cotton should rapidly absorb the acid for if the portion that is taken for immersion be but slowly absorbent, it is likely when but partly saturated to rise to the surface of the acid and on exposure to undergo the rapid decomposition technically called "firing." To secure the desired result the cotton should be free from oil, grease, and any protecting body. Their presence not only diminishes the absorptive power of the cotton but they, in common with the knots, tangles, cops, hulls, seeds, or similar foreign bodies, promote decomposition. It is a common practice to

[1] Read at the Brooklyn meeting.

use weaver's waste, or waste from the cotton gauze factories, in this manufacture on account of its cheapness and because it is found also that the thready form permits of ready handling in the hand-dipping and its compactness diminishes the amount of air which becomes entangled in the mass, as compared with that entangled in a similar mass of cotton "in the wool," and consequently the bouyancy of the mass is less.

Such waste necessarily becomes soiled with oil or grease, to a greater or less degree, during the carding and spinning, and it may contain besides knots, cops, tangles, and foreign bodies of various kinds, which latter are removed by means of the picker, while the oil and grease are removed by boiling with soda lye. Hence in determining the relative value of various samples of cotton offered for purchase, the relative amount of the grease, foreign bodies, and waste to be removed and of knots and tangles present, together with the general cleanliness of the sample, are to be considered.

Based on considerations such as these, the method of inspection is as follows:

1. Optical examination for color, cleanliness, presence of cops, knots, tangles, and foreign bodies, and for relative length and strength of fiber.

2. Odor.

3. Moisture, which is determined by drying a portion at 100° C. to constant weight.

4. Ether extract, which is determined by subjecting the weighed sample to the action of petroleum ether (boiling-point 50°–80° C.) in a Soxhlet extractor until the sample ceases to lose weight. The method of procedure is to expose the weighed sample in a light glass basket to ten automatic exhaustions, when it is removed, dried, and weighed. It is then returned to the extractor and subjected to five automatic exhaustions, when it is again dried and weighed. If it has lost weight by the last treatment the basket and contents are again returned to the extractor and exhausted three times and this treatment is repeated until the weight becomes constant.

The weight of the samples taken in the experiment varied between one and one and a half grams and the extractor had a

capacity of forty cc. for each automatic exhaustion. The ether extracts the oily matters in the cotton, both those which occur naturally and those which it has absorbed in the processes to which it has been subjected.

5. Soda-lye extract, which is determined by boiling the weighed sample for eight hours in a solution of sodium hydroxide of the same strength and in the same proportions as that used in the factory in the first boiling tub. For this purpose the waste, if in long bundles, is cut into pieces about one inch long, and ten grams of it placed in a beaker of about a half liter capacity, 104 cc. of a solution of caustic soda containing 17.305 grams to the liter (thirty-five pounds to 250 gallons of water) are poured upon it and the boiling carried on for eight hours, fresh water being added from time to time to keep the solution at constant volume. At the end of eight hours the liquid is poured off and the sample placed in a cotton filter, where it is squeezed and washed with hot water until the wash water gives no alkaline reaction. The sample is then dried to constant weight.

6. Ash, which is determined by placing from one to one and a half grams of the sample in a weighed platinum crucible pouring melted paraffin upon the mass, igniting it from the top, allowing it to burn slowly until the flame dies out and then igniting the residue to constant weight.

7. Rate of absorption of water. In making this test a sample of the material is thrown or dropped lightly on the surface of distilled water and the time between when it touched the surface and when (through absorption of the water by capillarity) it sinks to the bottom noted. One of the requisites for cotton suitable for making smokeless powder is that it shall sink in two minutes. In these experiments the cottons were tested not only in the condition in which they were received but also after treatment with ether; after drying for moisture, and after boiling with soda-lye; all being in the dry state. The vessel used varied in diameter from three to six inches, while the temperature of the water varied from 20° to 25° C. These differences or that of the size and form of the pellet seemed to produce no effect, but special attention must be paid to having distilled

water with a perfectly clean surface. With the same sample of cotton there were considerable variations in the time of sinking to the bottom of the vessel although the time of becoming thoroughly saturated so as to become submerged at the surface was fairly constant. The fact that the mass remained at the surface after saturation was found usually to be due to a bubble of air entangled in the mass which bouyed it up, or, less often, to a small portion of the mass being non-absorbent. This condition was evident on inspection as the non-absorbent portion of the sample remained opaque, while the absorbent portion appeared translucent. When the absorption failed to begin at once it usually did not take place at all, even after twenty-four to forty-eight hours exposure, or even when the whole mass was forcibly plunged beneath the water, in fact in these cases there seemed to be an actual repulsion between the water and the fiber. As what we seek to learn by this test is the relative rates at which the cottons tested will suck up the mixed acids during dripping, it would seem sufficient to note the moment at which they become thoroughly wet and submerged beneath the surface.

The detailed results obtained with five samples submitted at one time are as follows:

1. *Sample 1.*—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt and rust spots. Strong fiber.

Sample 2.—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt. Very strong fiber.

Sample 3.—Off white, yellowish tint. Long threads, freer from tangles than *1* or *2*. Free from dirt. Strong fiber.

Sample 4.—White. Partly short threads and partly loose fiber as if picked. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few rust spots.

Sample 5.—White. Whole fibrous and wooly, as if picked, the fibers being not over an eighth of an inch in length. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few dark specks.

2. *Sample 1.*—Faint odor of oil.
" *2.*—Very faint odor of oil.
" *3.*—Marked odor of oil.
" *4.*—Very faint odor of oil.
" *5.*—Very faint odor of naphtha (?)

The percentages of moisture, ether extract, soda-lye extract, and ash, (*3*, *4*, *5*, and *6*) are given in the following table:

Sample No.	Moisture.	Ether extract.	Soda-lye extract.	Soda-lye extract less moisture and ether extract.	Ash.
1.	4.93	0.97	9.16	3.26	0.86
2.	4.79	0.49	10.36	5.08	0.75
3.	5.17	1.20	9.26	2.80	0.80
4.	4.36	0.53	13.69	8.80	0.61
5.	4.69	0.09	7.58	2.80	0.40

7. The rates of absorption of water found was as follows:

Sample No.	Original condition of sample. Min. Sec.	After exhaustion with petroleum ether. Min. Sec.	After boiling in soda-lye. Min. Sec.	After drying for moisture determination. Min. Sec.
1.	∞	∞	2 00 1 00 2 00	∞
2.	∞	∞	2 00 1 00 1 40 50 3 30	∞
3.	∞	∞	∞	∞
4.	3 15 5 15 1 15	60 45	10 8 7 4	3 00 4 00 7 45
5.	∞	45 45 20 43	10 4 4	∞

∞ No submersion after twenty-four hours' exposure.

The appearance of the ash and of the soda-lye after extraction are worthy of notice. In samples 1, 2, and 3, the ash obtained was of a light green color, the green portion being soluble in water, leaving a yellowish residue, which was insoluble. The ash of samples 4 and 5 was reddish. The color seemed to be due,

in each case, to iron, it being in the ferrous condition in the first three cases and the ferric in the last two. As the latter evidently have been bleached with chlorine, this treatment would naturally oxidize the iron.

Soon after boiling the lye with the cotton began, the former, which was colorless at the start, began to acquire a color which increased in intensity for some hours. In the case of samples 1, 2, and 3, the lye, when the operation was finished, was of a pale sherry wine color, No. 4 was of a port wine color, while No. 5 was of a deep sherry wine color.

From this examination the samples are divided into two classes, *viz.*: cop waste and short fiber, treated cotton. Samples 1, 2, and 3 being in the first class and samples 4 and 5 in the second.

The short-fibered cotton cannot be nitrated successfully with the usual appliances and the presence of chlorine is objectionable as the cellulose nitrates produced from such cotton cannot be washed neutral.

Of the cop wastes, which are adapted to our present methods of manufacture, sample 1 seems on the whole to be the best, though it is but little superior to sample 2.

From the observations made it was found that in eighteen samples of cotton waste—

The moisture varied from 3.38 to 8.40 per cent.

The ether extract from 0.00 to 7.10 per cent.

The soda-lye extract from 3.53 to 5.36 per cent.

The ash from 0.05 to 1.79 per cent.

The rate of absorption after soda-lye extraction from one second to over twenty-four hours.

A sample of cottonseed lint gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
6.16	2.35	28.54	4.83	∞

A sample of waste cotton gauze gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
7.37	0.50	3.89	.95	7 seconds.

The rates of absorption quoted are for samples dried after receiving the soda-lye treatment. As indicated above, observations were also made on the original sample and after treatment

with ether, both after drying. The highest rate was obtained after boiling with soda-lye; many samples being still non-absorbent after treatment with ether.

Treatment with the soda-lye even improved the absorbent power of the samples of "Absorbent Cotton" submitted for testing the rate being increased from three seconds for the dried, untreated cotton, to one second for that which had been treated.

Experiments were made on the absorptive capacity of the cotton, and in one case a six-gram sample of absorbent cotton was found to retain ninety-three grams of water or 15.5 times its own weight.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY No. 8.]

REDUCTION WITH MAGNESIUM AMALGAM.

BY HERMANN FLECK AND LEWIS L. BASSETT.

Received August 21, 1895.

THE subject of neutral reducing agents has been taken up in a recent publication by J. B. Cohen and R. Ormandy.[1] The study of the same subject has been carried on in this laboratory during the past year. For this purpose magnesium amalgam, two per cent., was prepared in the following manner:

The required amount of mercury is placed in a small Hessian crucible and half covered with magnesium powder. The lid is put on loosely and the blast applied until a loud hissing noise begins. Once begun the reaction takes place by itself. This is repeated until the requisite quantity of magnesium powder has been added. A more uniform mass is obtained by boiling mercury in a hard glass tube, open at one end; then adding the magnesium in small quantities and shaking vigorously after each addition. The product is a silver white, crystalline, pasty mass which decomposes water with great energy and evolution of heat, and which upon exposure to air becomes covered with a black mass; probably a lower oxide of magnesium.

MAGNESIUM AMALGAM AND HYDROCYANIC ACID.

Two hundred cc. of ninety-six per cent. alcoholic solution of hydrocyanic acid containing eight grams of the acid were placed

[1] *Ber. d. chem. Ges.*, **27**, 1505.

in a liter distilling bulb connected to a condenser by a rubber tube. The condenser, by means of a long glass tube, led into a flask containing dilute hydrochloric acid, and this in turn was attached to a suction pump. After cooling in a mixture of ice and salt a small quantity of the amalgam was introduced into the neck of the distilling bulb, the cork replaced, and by a sharp jerk introduced into the liquid. When the theoretical amount of two per cent. amalgam had been introduced the contents were directly distilled into dilute hydrochloric acid evaporated to dryness, redistilled with addition of caustic soda into dilute hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. A small amount of ammonium chloride remained, produced by the action of hydrochloric acid upon the unconverted hydrocyanic acid.

The yield was fifteen per cent. 0.1122 grams methylamine platinichloride gave 41.08 per cent. platinum, the theory being 41.24 per cent. With more than the theoretical amount of amalgam a larger yield can surely be obtained.

MAGNESIUM AMALGAM AND BENZONITRILE.

Ten grams benzonitrile were dissolved in 200 cc. of ninety-six per cent. alcohol and twice the theoretical amount of amalgam added under the same conditions as above. The reaction product was filtered on a suction pump from the magnesium hydroxide formed and evaporated to dryness with hydrochloric acid, caustic soda added and extracted three times with ether. The ethereal solution was evaporated with hydrochloric acid to dryness and the residue extracted with absolute alcohol. There remained one gram of a crystalline substance melting under 100° C., whose alcoholic solution immediately reduced platinic chloride. This substance, possibly of a hydride nature, will be further investigated.

MAGNESIUM AMALGAM AND ACETOPHENONE.

Ten grams acetophenone were dissolved in fifty cc. ether and somewhat more than the theoretical quantity of amalgam added. When the mass cakes, alcohol is added and then sufficient water to completely decompose the amalgam. Dilute hydrochloric acid is added to dissolve the magnesium hydroxide formed, and

the semi-crystalline mass extracted with ether, the ethereal solution evaporated to dryness, crystals formed freed from oily substance by washing with ligroin, and recrystallized from benzene.

Of the products theoretically possible, acetophenone pinacone, or diphenyl dimethyl glycol, forms large colorless prisms, melting at 120° C. The product obtained melts at 120° C., and in every particular corresponds to the above. The yield was excellent.

It is our intention to further pursue the investigations with nitriles, ketones, oxynitriles, and amido-nitriles.

UNIVERSITY OF PENNSYLVANIA.

TWO DEFINITE CARBIDES OF IRON WITH CHROMIUM (MOLYBDENUM AND TUNGSTEN).

BY JAMES S. DE BENNEVILLE

Received September 6, 1895.

A PREVIOUS paper[1] described in detail the results of a chemical examination of some ternary alloys of iron with chromium, molybdenum, and tungsten. In the course of the experiments there described two definite carbides were separated and it is proposed to give additional details obtained later. The physical description of the crystals is taken from Professor F. Lynwood Garrison's discussion of the paper cited.[2] The alloys described were made by taking pairs of the elements: tungsten chromium irons, molybdenum chromium irons, and molybdenum tungsten irons. The proportions taken were not based on equal weights but on quantities taken in the ratio of the atomic masses of the constituents. They were 1:1, 5:1, and 1:5. A lump of cast iron weighing fifty grams was imbedded in the mixture and melted, a white heat being maintained for an hour. The aggregations to be described were found in the chromium alloys and only in the two alloys (Nos. II and V) in which chromium was the predominant metal. These two alloys showed well individualized crystals differing in form and reactions from the matrix in which they were imbedded.

[1] Iron and Steel Institute, May meeting, 1895.

[2] *Ibid.* I take this opportunity of expressing my indebtedness to Professor Garrison, through whose kind offer I was enabled to present this paper to the council of the Institute.

Berthier and also Percy[1] have noted the presence of needle-shaped crystals in ferrochromium and in chromium steels. Further details are not given. Behrens and Van Linge, in a recent paper, have described at length the physical and chemical properties of segregations in ferrochromium. On treating the alloy with acid they obtained bayonet or rod-shaped crystals, three to four millimeters in length, a few being eight to ten, non-magnetic, of hardness 7.5. The composition, however, varied with the ferrochromium from which they were obtained; ferrochromium with 13.8 per cent. chromium, eighty-one per cent. iron, and five and one-half per cent. carbon, giving the compound $Cr_2Fe_7C_3$, whereas with fifty per cent. chromium, the composition was approximately Cr_2FeC_2. They point out the relation of the first compound to Fe_3C, chromium replacing a part of the iron, and consider that chromium forms "double carbides less soluble in iron than the ferrocarbides, at the same time facilitating the crystallization of the latter."[2]

Considering the marked development of the segregations in the ternary alloys it appears to me doubtful whether they are to be referred, as to origin, to the iron carbides. The prismatic form is not a dominant one with the iron carbides, although it is found under certain conditions. Howe, citing Sorby, notes three successive crystallizations in hard cast-steel. I quote him in *extenso*: he says, "First we have the large prismatic columnar crystals, normal to the cooling surface, and conspicuous on fracture. They apparently represent the first crystallization, be it of hardenite, be it of the hypothetical mother-of-pearlyte, which in this case has expelled the excess of cementite present, distributing it as an elongated meshwork between the crystals. Secondly, these columns or crystals are chiefly composed of groups of pearlyte, disposed with little or no relation to the columnar structure, indeed shooting from one column into another, and apparently formed from the substance of the primary crystals of a second crystallization. Finally, by a third crystallization, each of the individual members of the radial

[1] Percy, *Iron and Steel*, p. 186. Berthier from Percy not the original.

[2] Recuil trav. chim. Pays-Bas., **13**, 155-181. From the abstracts in *J. Soc. Chem. Ind.*, **14**, 275, *1895*, and *J. Chem. Soc.*, **64**, 452, *1894*.

groups of pearlyte has split into parallel layers of cementite and ferrite, which apparently occupy the space previously occupied by a simple undivided crystal." Again, "the exterior columnar structure is clearly due to the rapid escape of heat from the shell of the ingot into the mold. We may suppose that the metal naturally tends to crystallize in equiaxed grains: that there is a struggle between this tendency and the tendency to crystallize in indefinitely long prisms which the rapid cooling sets up. As the walls thicken and the flow of heat outward slackens, the prismatic tendency weakens: the sudden transition from the prismatic to the equiaxed formation suggests that no resultant, no compromise is possible, so that from the moment when the equiaxial tendency outweighs the prismatic it reigns alone, as if its rival were not."[1] This is the only mention of prismatic structure in ordinary carbon steel that I find in the "Metallurgy." If the intense hardness of ferrochromium, ferrotungsten, and ferromolybdenum is to be ascribed to the conversion of the carbon present into hardening carbon and its retention in that form—although from the researches of Riche and especially of Moissan this hardness can just as well be attributed to carbides of chromium, tungsten, or molybdenum—the alloys under discussion can be justly compared to hard cast-steel containing a large excess of carbon and the prismatic form of the crystals in II and V could be attributed to a structure found in such steel as described above. However, the conditions are by no means identical. The crystals in II and V are present throughout the mass forming a network with the interstices filled in by the equiaxial granular material. There is no line where the equiaxial tendency has overcome the prismatic and so sharply differentiated the alloys into an external prismatic shell surrounding an interior of equiaxed grains. Also, the crystals show a marked increase in density as compared with the granular material and the alloys in which they are found differ in hardness from the rest of the series. In fact, the crystals give every evidence from their sharpness of outline of having a higher freezing-point and as having separated out from the mass of the alloy at a time when it was not liquid enough to effect their

[1] Metallurgy of Steel, p. 182, 183.

segregation into any one portion of the alloy, but liquid enough to secure their own crystalline form at the expense of compounds crystallizing later. For when a mass of iron is allowed to cool uniformly, from the resultant structure it would appear that the constituent compounds have freezing points not so far removed from each other as to effect the segregation of any one of them into a part of the mass. This has no reference to the microstructure of iron and steel in which the compounds identified appear to be somewhat unstable in nature, passing readily from one form to the other even by cold working. The columnar structure is only stable under the limited conditions existing for its formation and by slight alteration of the method of cooling or of working passes readily into other forms. Also, the columns are often distinctly a mere structural arrangement of the granular material with radial lines forming prismatic aggregations in which the granular components are distinctly manifest. There is in the micro structure of steel a compound to the development of which might be attributed the prismatic and needle-like form when found in iron alloys. This has been described by Osmond[1] and named by him martensite. It is found in steel of 0.45 carbon heated to 825° and tempered at 720° in a cooling mixture of —20°. It occurs "in groups of needles or rather of rectilinear fibers lying parallel and separated or not by a granular or vermicular filling." From the grouping of three systems of fibers respectively parallel to the three sides of a triangle he regards them as crystallites of the cubical system. In the absence of any other source the form of the prismatic needles found in ferrochromium and in these tungsten chromium irons (II) and molybdenum chromium irons (V) could be attributed to the development of the microstructural element, to the fixation of the prismatic columnar structure, or to the rod-shaped fiber structure of Abel's carbide Fe_3C. As to the two first, in despite of their instability and the absence of any boundary line between the prismatic and granular formations, it seems to me better to attribute the form to the carbide of chromium isolated by Henri Moissan.[2] This carbide, of formula CCr_4, he describes

[1] Bull. de la. Soc. d'Enc. pour. l'Ind. Nat., May, *1895*.
[2] Bull. Soc. Chim. Paris, 11, 1016, *1894*.

as forming needles one to two cm. in length lining the cavities found in the melt. He also isolated a carbide C_2Cr_3 occurring in brilliant lamellae. Of the two the lamellar carbide was the harder, scratching topaz but not corundum, whereas the prismatic carbide scratched glass readily, but quartz only with difficulty. Both carbides were very stable compounds and were chemically inert. The crystals found in the ternary alloys were confined to the high chromium compounds in which the ratio of chromium to tungsten or molybdenum was as five to one. The alloys, II and V, were much softer than the other alloys, which would be the case if hardness is dependent on the carbide of chromium present. For comparison, Table I gives the composition of the series of alloys.

If now the prismatic segregations in ferrochromium be compared it will be found that, with the exception of the compound $Fe_7Cr_3C_2$, chromium is the dominant constituent in the carbide. For example :

TABLE II. SEGREGATIONS IN FERROCHROMIUMS.

	B. and Van L. $Fe_7Cr_3C_3$.	B. and Van L. $FeCr_2C_2$.	V. Analysis 1 $Fe(CrMo)_6C_4$.	V. Analysis 2. $Fe(CrMo)_6C_4$.	II. $Fe(CrW)_6C_4$.	II B. $Fe(CrW)_6C_4$
Iron	0.8100	0.3030	0.4639	0.4650	0.4724	0.4723
Chromium ..	0.1380	0.5671	0.4623	0.4606	0.3542	0.3682
Molybdenum	....	....	0.0201	0.0194	....	....
Tungsten ...	....	....	....	....	0.1139	0.1007
Carbon	0.0550	0.1299	0.0553	0.0559	0.0595	0.0599

$Fe_7Cr_3C_3$, on the contrary, could fairly be classed as derived from an iron compound—Fe_3C. This compound, isolated by Abel and subsequently by Muller, is described as a dark-grey residue; Osmond and Werth obtained it in the form of bright plates; Behrens and Van Linge treating Dannemora iron, obtained it as bright spangles and rods; and Arnold and Read obtained it in two forms, as bright silver plates and as a grey black powder in microscopic granules.[1] The segregations in the ternary alloys are to be compared with the "brilliant white radial needles" described by Behrens and Van Linge and which

[1] Abel—Proc. Inst. Mech. Eng., *1895*, p. 30; Muller—Stahl und Eisen, No. 5; Osmond and Werth—Annales des Mines *1895*; Behrens and Van Linge—as cited, *1894*; Arnold and Read—*J. Chem. Soc. Trans.*, 65-788, *1894*. Also Ledebur Jour. Iron and Steel, Inst. 1893, II. 53. The quotations following are from the abstract of Behrens and Van Linge's paper.

TABLE I. COMPOSITION OF THE ALLOYS. *J. Iron and Steel Institute*, I, 1895.

ALLOY	I	II	III	IV	V	VI
Total carbon	0.0317	0.0299	0.0311	0.0323	0.0312	0.0323
Carbon evolved by hydrochloric acid	0.0122	0.0074	0.0127	0.0104	0.0084	0.0130
Carbon in hydrochloric acid residue	0.0195	0.0225	0.0184	0.0219	0.0228	0.0193
Carbon in nitric acid residue	none	Table VIII	none	none	Table VIII	none
Silicon evolved by hydrochloric acid	0.0033	0.0142	0.0072	0.0075	0.0055	0.0022
Silicon in hydrochloric acid residue	0.0193	0.0083	0.0130	0.0103	0.0119	0.0051
Phosphorus evolved by hydrochloric acid	0.0019	0.0025	0.0012	0.0014	0.0020	0.0003
Phosphorus in hydrochloric acid residue	0.0009	0.0007	0.0003	0.0006	0.0005	0.0020
Manganese	0.0004	0.0043	0.0049	0.0013	0.0027	0.0004
Sulphur	——	.....	.....	.....	.....	.....
Chromium	0.0846	0.1207	0.0211	0.0802	0.2257	0.0485
Tungsten	0.3382	0.0440	0.2125	.....	.....	.....
Molybdenum	——	.....	.....	0.1184	0.0735	0.3065
Iron	0.5197D	0.7754D	0.7087D	0.7531	0.6470D	0.5999
Specific gravity	11.010	7.995	10.257	7.571	7.300	8.410
Formula	$Fe_{45}Cr_7W_8$	$Fe_{82}Cr_{10}W$	$Fe_{34}CrW_3$	$Fe_{48}Cr_6Mo_4$	$Fe_{65}Cr_{23}Mo_4$	$Fe_{25}Cr_9Mo_7$
Condensation from composition difference	2.051+	0.453+	1.869+	0.089+	0.054—	0.963+

ALLOY	VII	VIII	IX	Cast iron used.	Chromium for steel.	Tungsten for steel.
Total carbon	0.0335	0.0289	0.0290	0.0331	0.0773	0.0343
Carbon evolved by hydrochloric acid	0.0162	0.0126	0.0147	0.0039	.....	0.0014 nitrogen
Carbon in hydrochloric acid residue	0.0173	1.0163	0.0153	0.0292	.....	.....
Carbon in nitric acid residue	none	none	none	0.0286	.....	.....
Silicon evolved by hydrochloric acid	0.0073	0.0184	0.0023	0.0030	total	total
Silicon in hydrochloric acid residue	0.0097	0.0067	0.0049	0.0194	0.0144	0.0039
Phosphorus evolved by hydrochloric acid	0.0014	0.0017	0.0018	0.0020	total	total
Phosphorus in hydrochloric acid residue	0.0006	0.0013	0.0006	0.0004	0.0012	trace
Manganese	0.0003	0.0019	0.0034	0.0071	trace	none
Sulphur	.....	.....	.....	0.0003	.....	.....
Chromium	.....	.....	.....	.....	0.8995	.....
Tungsten	0.1471	0.1940	0.3066	.....	.....	0.9593
Molybdenum	0.0949	0.1346	0.0379	.....	.....	.....
Iron	0.7012	0.6086	0.6189	0.9347D	0.0079	0.0007
Specific gravity	11.154	11.384	12.365	7.474	5.103	15.175
Formula	$Fe_{68}Mo_6W_4$	$Fe_{34}Mo_4W_3$	$Fe_{120}Mo_4W_{17}$	.....	.....	.....
Condensation from composition difference	2.898+	2.942+	3.438+	.....	.....	.....

=by difference.

are characteristic of ferrochromium, attaining a very marked development which places them entirely outside the category of micro or sub-micro structure. I am in doubt as to whether the formula $Fe_7Cr_2C_3$ is meant to represent the needles, for this compound is described as "a coarse brownish grey lustrous powder, made of small bars, of which many are three to four mm. in length." The data are confessedly very scanty but against the iron derivation of the needles is to be placed the three compounds found in the ternary alloys whose constancy can hardly be ascribed to the constituent tungsten or molybdenum, metals chemically to be classed with chromium; and the existence of Moissan's carbide Cr_4C, an analogous compound. This is more clearly understood from Professor Garrison's description given later. That, however, the constitution of such compounds would be dependent on the composition of the mixture and would only be fairly constant within certain limits can be readily understood, as, for example, with double salts crystallizing in varying proportions; and hence when the iron becomes an unimportant factor in the composition of the alloy its influence would correspondingly wane in the compound crystallizing from the mixture, and vice versa. It is to be noted, moreover, that very little is known of the valence or combining power of the elements in metallic alloys and not only is this lacking for iron and chromium, but if the composition of the crystals is dependent on the composition of the alloy and the temperature at which they separate there may also be an alteration in the ratio in which iron and chromium combine, for valency may well be dependent on the temperature. Note that alloy II contains 12.07 per cent. of chromium but has a much greater content of chromium in the separated crystals than the compound of formula $Fe_7Cr_3C_2$.

The separation of the crystals from the granular material was readily effected by the comparatively slight action of nitric acid which left the crystals as residue intermixed with a little silica. This was volatilized as silico-fluoride and after washing with water and subsequently with ninety-five per cent. alcohol the crystals were obtained free from impurity. Their reactions show them to be chemically very inert compounds. As stated, they are but little attacked by nitric acid, strong or dilute.

Hydrochloric or hydrofluoric acid does not attack them. Strong sulphuric acid slowly decomposes them leaving a black residue which still retains the form of the crystals. The solvent is useless as a means of analysis. By themselves the crystals are attacked but slowly by strong aqueous solution of bromine or of iodine and only on heating. However, in the residue obtained by treating the allow with these reagents no trace of the crystals could be observed, using a lens magnifying fifty diameters. With reflected light the residues showed granular masses of irregular shape with brilliant metallic luster. From the mode of occurrence of the crystals in the alloy they could hardly have been absent from the samples examined. At a red heat chlorine, bromine, and iodine readily decompose them, but their analysis is best effected by fusion with an oxidizing mixture of sodium carbonate and saltpeter with addition of caustic soda.

Professor Garrison, in his discussion,[1] gives the form and dimensions of the crystals as follows: "I have examined under the microscope the segregations obtained from alloys II and V and find them to consist of well developed prismatic hexagonal crystals, more or less corroded by the nitric acid solvent. I was not able to detect any of the crystals with pyramidal terminations; most of them appeared to have been broken, leaving ragged ends, as would be observed in Figs. 1 and 2. The general appearance of the crystals from the different alloys is similar. Those from II averaged 0.03 to 0.04 of an inch in length, and 0.003 of an inch in diameter; those from V were 0.03 to 0.04 in length and 0.005 of an inch in diameter. The aspect of the crystals under a magnification of thirty-five diameters is well shown by the micro-photographs; Fig. 1 being from alloy II, and Fig. 2 from V, I was able to detect a slight difference in color between the two varieties when they were heaped in masses and held in the proper light. II had a decided yellowish metallic luster; V a dark steel-grayish-blue color and luster. The slight difference in thickness was not appreciable to the naked eye, neither would the color or luster be apparent to a casual observer. I experienced some difficulty in making the specific gravity determinations of these crystals, owing to

[1] Iron and Steel Institute, May meeting, 1895.

the extremely small quantities. On the whole, I think those mentioned are nearly correct, although that of II might be a light one." Of II specific gravity is 12.80; of V 7.473 (Garrison).[1]

The analytical results obtained were:

Alloy V.—Ferromolybdenumchromium Carbide. The analysis was made as follows: Half a gram of pure crystals were fused with the oxidizing mixture with addition of caustic soda. The melt was cooled, lixiviated in water, and the solution containing chromate and molybdate filtered from the residual ferric hydroxide. The solution was acidified with hydrochloric acid and boiled to dryness with addition of alcohol to ensure reduction of the chromic salt. The residue was then dissolved in a little dilute hydrochloric acid, diluted and brought to boiling. Chromium was precipitated by ammonia in excess, the boiling being continued for at least half an hour. The precipitated chromic hydroxide was filtered off, washed twice with hot water, dissolved in dilute hydrochloric acid, and reprecipitated by ammonia. This solution was filtered, the filtrate being added to the first but not the washings. The chromic hydroxide was now thoroughly washed by boiling up with water, decanting, finally throwing on the filter, and washing with boiling water. It was then dried, ignited, and weighed as Cr_2O_3. In analysis 1 (table II) the filtrate containing the molybdenum was boiled until the odor of ammonia had to a great extent disappeared. The solution was then acidified with sulphuric acid, poured into a separatory funnel containing zinc and, after reducton, titrated with permanganate (Pisani's method). In analysis 2 the molybdenum was determined gravimetrically. The ferric hydroxide was examined for silica but the quantity found checked closely with that present in the alkali salt used for fusion. After removal of platinum, iron was converted to sulphate and titrated in acid solution by permanganate. The chromic oxide was fused with bisulphate and the solution examined for phosphorus with nega-

[1] In some experiments carried out by Professor Garrison and myself with highly phosphoric titaniferous pig iron, prismatic needles were obtained lining the cavities and blow-holes. Their form could not be made out with certainty but they were well developed and in no sense belonged to the micro structure of the alloy. They have not yet been isolated. The prismatic form is of frequent occurrence in Ferromanganese.

tive results. If silicon or phosphorus were important constituents of the crystals they would readily be detected in a half gram sample. The carbon of analysis 1 was determined by direct combustion of the crystals with the lead and potassium chromate mixture. The carbon of 2 was determined by combustion of the residue obtained after first decomposing in chlorine at a red heat.

TABLE III. FERROMOLYBDENUMCHROMIUM CARBIDE.

	Analysis 1.	Atomic ratio.	Analysis 2.	Atomic ratio.
Iron	0.4639	0.828	0.4650	0.830
Chromium	0.4623	0.882	0.4606	0.879
Molybdenum	0.0201	0.021	0.0194	0.020
Carbon	0.0553	0.461	0.0559	0.464

No manganese, silicon, or phosphorus were present. These results give the ratio Fe : CrMo : C :: 1.79 : 1.95 : 1, or formulated $Fe_7(CrMo)_8C_4$. To this compound I give the name Wahlite, from Dr. William H. Wahl, well known for his valuable contributions to metallurgy.

Alloys II and II B.—*Ferrotungstenchromium Carbide.* In addition to the alloy (II) described in the first paper, a second alloy (II B) was made using 200 grams of iron in the melt instead of fifty. The object in doing so was to determine whether change in composition of the melt had any effect on the composition of the resultant crystals. The quantity of crystals obtained for analysis II was small. Iron, chromium, and tungsten were determined after purifying by nitric acid one gram of the original material. The residue was then analyzed and the calculations made to 100 per cent. For analysis II B abundant material was available. Considering the small quantities available for the first analysis the agreement is satisfactory. Comparing with alloy V it would appear that the ratio of chromium to iron is not the same in the two alloys. Tungsten and molybdenum probably play the same rôle as chromium and replace it perhaps in varying quantities. The analysis was made by decomposing the crystals as with alloy V. The solution containing tungstate and chromate was acidified with hydrochloric acid, alcohol added, and evaporated to dryness. The residue was taken up in dilute hydrochloric acid and an equal bulk of alcohol added.

The tungstic acid was filtered off, dissolved from silica by ammonia, the solution evaporated, and tungsten determined as WO_3. The filtrate containing chromium was brought to boiling and chromium hydroxide thrown down by ammonia. Alloy II, as obtained in original sample, contained iron 0.0423, chromium 0.0317, tungsten 0.0102. The analytical results gave :

TABLE IV. FERROTUNGSTENCHROMIUM CARBIDE.

	Alloy II.	Atomic ratio.	Alloy II B.	Atomic ratio.
Iron	0.4724	0.843	0.4723	0.843
Chromium	0.3542	0.676	0.3682	0.702
Tungsten	0.1139	0.060	0.1007	0.054
Carbon	0.0595	0.496	0.0599	0.494

No manganese, silicon, or phosphorus was present in II B. These results give the ratios :

Alloy II. Fe : CrW : C :: 1.69 : 1.49 : 1, or formulated $Fe_7(CrW)_6C_4$.

Alloy II B. Fe : CrW : C : : 1.73 : 1.53 : 1, or formulated $Fe_7(CrW)_6C_4$.

Carbon in both cases was determined by direct combustion of the crystals. To the compound I give the name Garrisonite, from Professor F. Lynwood Garrison, a valued contributor to the study of the microstructure of iron and to its metallurgy. Alloy II B contained, chromium 0.1070, tungsten 0.0871.

ON THE POSSIBILITY OF THE OCCURRENCE OF HYDROGEN AND METHANE IN THE ATMOSPHERE.[1]

Received September 9, 1895.

BY FRANCIS C. PHILLIPS.

WHATEVER may have been the process by which organic remains have in the course of time been caused to yield gas and petroleum, a considerable portion of the gas evolved in the early stages of decay must have escaped into the atmosphere before the burial of such remains under sedimentary deposits, and the consequent imprisonment of the more volatile products could have occurred. This would have been the case if, as in the view of the older geologists, the source of gas and oil is to be looked for in the slow decomposition, at low temperatures, of

[1] Read at the Springfield meeting.

masses of seaweeds as they were gradually buried under accumulating sediments. It would have occurred likewise if, according to Engler's hypothesis, gas and oil have come from the distillation of animal remains under pressure of overlying sediments and at a gentle heat.

For a long interval of time must have elapsed between the commencement of decay and the final burial of such remains under marine deposits, of sufficient thickness and compactness, as to cause the retention of the hydrocarbons until the sediments became consolidated into rock.

In a paper upon the origin of natural gas[1] I have called attention to the great difference in the nature of the changes which may occur in organic remains submerged under water and protected from atmospheric influences. The early stages of the decay are rapid, and much hydrogen may be produced. The later stages are more gradual, and methane may be a chief product of the decay. At the beginning of the process the cell contents are chiefly concerned in the change. Even if buried under deep sediments the tumultuous nature of the gas evolution must cause the gas bubbles to break through and escape from dense masses of clay and sand.

The following experiment was described in the paper cited: A quantity of a seaweed was allowed to decay under water in an apparatus so constructed that any gas produced could be collected over mercury. Rapid decomposition soon set in and continued for ten days, when the evolution of gas apparently ceased, having become much retarded towards the end. In all 803 cc. of gas were collected. Analyses were made of the first portion of 300 cc., of a second portion of 300 cc., and of a third portion of 203 cc. The results are tabulated below:

	First portion.	Second portion.	Third portion.
Carbon dioxide	18.23 per cent.	32.47 per cent.	53.44 per cent.
Carbon monoxide	0 "	0 "	0 "
Ethylene	0 "	0 "	0 "
Methane	0.30 "	0.28 "	0.08 "
Hydrogen	62.24 "	48.97 "	42.02 "
Nitrogen	19.23 "	18.28 "	4.46 "
	100.00	100.00	100.00

[1] *Am. Chem. J.*, 16, 417.

The temperature during the experiment did not exceed 20° C.

The same apparatus was kept in position for two and one-half years after the above experiment was made. During this time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 cc. of gas had collected. This was found to consist of methane.

Frankland & Jordan[1] found that grease left to decay under water, air being excluded, evolved gas of the following composition:

	In 3 days.	In 3 days.	In 4 days.
Carbon dioxide	84.63	87.66	84.41
Oxygen	0.13	....	....
Hydrogen	6.90	8.75	9.17
Other combustible gases	2.51	0.71	0.27
Nitrogen	5.83	2.88	2.15

I have examined gas collected from swamps in many localities. Gas samples have been taken from streams having muddy bottoms and in which vegetable remains had accumulated. Carbon dioxide, nitrogen and methane are usually found in shallow swamps. In deeper swamp waters, where masses of vegetable debris of greater thickness occur, hydrogen is often found in small quantities mixed with carbon dioxide, nitrogen and methane.

According to the hypothesis of Mendeleeff natural gas and petroleum have been produced by the action of steam at high temperatures upon the metallic compounds of carbon.[2] The general result of experiments upon the action of steam upon the heated carbides of iron, manganese and other metals, has been to show that in all such cases there is produced mainly hydrogen mixed with relatively small quantities of hydrocarbons. It is found, however, that the natural gas which flows from the wells of Pennsylvania, New York, West Virginia, Ohio, and Indiana, consists mainly of methane with small quantities of other hydrocarbons, but does not contain free hydrogen. Hence if we accept the hypothesis of Mendeleeff we must suppose that the natural gas, now flowing from the earth in such vast quantities, represents the diminished residue of a much larger volume

[1] J. Chem. Soc. (Lond.) 1883, p. 295.

[2] Mendeleeff: Principles of Chemistry, 1, 365.

of gas from which the free hydrogen has escaped through the overlying rocks. Whatever view is adopted as to the origin of natural gas there seems to be good reason to believe that considerable volumes of hydrogen and of gaseous paraffins have found their way into the atmosphere, and that the process has been continuous since early geological times.

Evolution of carbon dioxide from organic remains is merely one stage in a cycle of changes. The carbon dioxide present in the atmosphere parts with its carbon to growing plants. They, in their turn, yield back carbon dioxide as they die and decay. On the other hand each bubble of hydrogen and of methane, once set free at the earth's surface, probably escapes unoxidized and unabsorbed to ascend into the higher strata of the atmosphere.

Of all the forms which hydrogen and carbon can assume in nature, free hydrogen and methane are among the most stable and unalterable as regards all influences at the earth's surface. Their slight solubility in water protects them still further from oxidation.

In the natural gas regions gas bubbles are easily produced by stirring up the sediments at the bottom in streams, ponds and rivers. This is not only the case where decaying vegetation occurs, but in streams flowing over gravel and pebbles where no decay is in progress. The loose gravel appears merely to arrest temporarily the gas on its way out from the earth and renders it visible as it escapes in bubbles through the water. If the gas accumulated under gravel and sand in streams be dislodged by stirring it is usual to find that, in a day or two, or even after a few hours, it has again collected in considerable quantity. Constant agitation of the gravel seems not to diminish the amount of the gas flow.

Such emanations of gas are common in Western Pennsylvania and Western New York, in regions where the occurrence of hard rock directly below the gravel bed of a stream precludes the supposition that the gas has resulted from the decay of recently buried tissues. It is probable that the gas which is continually accumulating in such situations is derived from great depths, that its presence is the result of a slow process of diffusion from

below, which only terminates as the gas enters the atmosphere, and that it constitutes a considerable portion of the natural gas which was stored originally in the rocks.

The feebly luminous flame produced by this gas distinguishes it from the nitrogen, which so frequently collects in the sands of river beaches in regions of constant fluctuations of water level due to tides, and where organic remains are abundant.

In the latter case the air penetrating the sand at low tide parts with its oxygen to the decaying matter, and as the tide rises again the residual nitrogen is expelled in bubbles under the pressure of the advancing water, while the carbon dioxide formed is retained in solution.

Gas collected from the gravel bottom of a stream flowing into the Ohio river near Sewickley, Pa., was found to have the following composition:

	Per cent.
Methane	93.06
Nitrogen	6.70
Carbon dioxide	0.24
	100.00

There is no reason to suppose that the diffusion of gas from the earth into the atmosphere is confined to surfaces covered by water, although it can only be made visible by the formation of bubbles in water.

It is no doubt continually in progress in regions of Devonian and carboniferous rocks.

This slow diffusion of gas from the earth into the atmosphere has occured since early geological times and in regions where erosion has finally carried away whole systems of sedimentary rocks, liberating the imprisoned hydrocarbons by slow degrees. The gas thus escaping from within the earth's crust is added to that which is derived from recent decay on the surface, and probably forms no inconsiderable part of the total quantity carried continually into the atmosphere.

Hydrogen in a limited volume of air follows the well-known law of diffusion, mixing completely with the air.

Should a large mass of hydrogen enter the earth's atmosphere, the case would be different. Hydrogen, while it would diffuse

laterally with the air, would tend to accumulate in the upper strata on account of the great difference between its specific gravity and that of the constituents of the air. Ferrel,[1] has fully discussed the hypothetical case of the occurrence and arrangement of a very light constituent in the atmosphere, "Where the relative densities of the constituents regarded as independent atmospheres, would be nearly the same at the different altitudes, as in the case of oxygen and nitrogen, a constant agitation of the whole may keep them so mixed up that the proportions are nearly the same at all altitudes; but, in the case of a very rare constituent, the tendency would be for it to rise up so far above all the others that it could not become mixed up with them except in the lower strata, and at a considerable altitude it would be the only sensible constituent unaffected by the agitation of the comparatively much denser constituents which would exist, only sensibly lower down, near the earth's surface."

If the presence of hydrogen is ever positively detected in the atmosphere, it must be looked for in air samples collected as far away from the earth's surface as possible.

An experimental demonstration of the presence or absence of hydrogen in air, would be of great interest if the method to be employed were certain as regards its results. Existing methods for the detection or determination of hydrogen when present in traces, are not satisfactory.

After many trials, I have devised a method for the detection of traces of free hydrogen in a gas mixture. The method consists, briefly, in passing the gas over anhydrous palladium chloride contained in a glass tube. Free hydrogen reduces this salt at once, and in the cold, being converted into hydrochloric acid, which is recognized by passage through a silver nitrate solution.

Having in palladium chloride a reagent of extreme delicacy for free hydrogen, it seemed to be of interest to attempt a test for hydrogen in air, and in order to avoid as far as possible, all danger of impurities from local conditions at the earth's surface, some experiments were tried on Mount Washington, New Hampshire, during August, 1892.

[1] Annual Report of the Chief Signal Officer of the Army for 1885, pt. 2, p. 41.

The elevation of Mount Washington, nearly 7000 feet, did not justify the belief that upon its summit strata of air materially different from those at sea level could be reached, but there was the undoubted advantage of greater purity and freedom from local contamination.

By permission of Mr. Mark Harrington of the U. S. Agricultural Department, a room in the Weather Observer's building on the mountain, was used for the purpose.

I desire here to express my appreciation of the courtesy shown by Mr. Harrington and also by Mr. Mitchell in charge of the station, in affording facilities for the work.

Details of the work are omitted, as the results of two very carefully conducted experiments were negative, and therefore did not lead to a definite conclusion.

It may be suggested that ozone, by reason of its great oxidizing power, would tend to prevent the accumulation of combustible gases in the upper atmosphere. Oxygen is well known to derive its active properties from the influence of the electric discharge.

Ozone may be produced locally in considerable quantity as a result of violent electrical disturbances in the atmosphere. Much of the ozone thus formed probably expends its power in oxidizing atmospheric nitrogen to nitrous and nitric acid.

Ozone has a specific gravity much greater than oxygen, and would, consequently, tend to descend rather than to rise to the outer limits of the atmosphere. While the production of ozone must occur at points remotely distant and at considerable intervals of time, the evolution of hydrogen and methane at the earth's surface is continuous. Moreover, thunderstorms only occur during a brief portion of the year in temperate climates, and are unusual at all times in far northern latitudes.

In view of these facts it seems improbable that ozone can be considered likely to materially retard an accumulation of the lighter gases, hydrogen and methane, in the upper atmosphere.

Hydrogen and methane are not oxidized by prolonged contact with a two per cent. solution of hydrogen peroxide at 20° C.

It is true that the upper air may contain nitrous acid. Paper coated with potassium iodide and starch was found to be rapidly turned purple when exposed on Mount Washington. Free

hydrogen is, however, not oxidized by fuming nitric acid[1] and it is hardly likely that nitrous acid, in the highly diluted condition in which it must be looked for in air, could cause an oxidation of hydrogen.

Meyer[2] and Askenasy found that on exposure to bright sunlight, a mixture of oxygen and hydrogen suffered no change. Combination did not occur even on exposure of the gas to a temperature of 600° C.

Meyer and Seubert[3] have shown that under highly reduced pressure combination does not occur in a mixture of oxygen and hydrogen under the influence of the electric spark. Experiments with mixtures of various hydrocarbons with oxygen, led to similar results. The minimum pressures at which the electric spark caused an explosion, were about one-tenth of an atmosphere in the case of hydrogen, and one-sixth of an atmosphere in the case of methane. In earlier times Humphrey Davy was led to similar conclusions as regards the explosion of rarified gas mixtures.

Although the minimum pressure at which chemical union would occur, may vary with the character of the discharge, it may be asserted that electrical disturbances are less likely to influence the oxidation of these combustible gases in the higher atmosphere where they must be looked for, if present in the atmosphere at all.

Methane and hydrogen possess under all conditions, great resistance toward oxidizing agents, and, once set free in air, it is questionable whether either gas could undergo any change by which it might be wholly brought back within the sphere of reactions produced by organic life, or by oxygen. Ferrel has suggested that the hydrogen of the sun's atmosphere may form merely an outer layer, resting upon much denser gases below.[4] It is possible, at least, that such an arrangement exists in the earth's atmosphere.

It seems desirable that tests for hydrogen and methane in air, should be made at still greater altitudes in order that more defi-

1 Winkler: *Ztschr. anal. Chem.*, *1889*. 269.
2 *Ann. Chem.* (Liebig), **269**, 72.
3 *J. Chem. Soc. 1884*, 587.
4 *Loc. cit.*

nite information may be gained upon this interesting subject, although serious difficulties would be encountered in attempting to reach an altitude so high as to render the results of chemical tests positively conclusive.

WESTERN UNIVERSITY LABORATORY,
ALLEGHANY, PA.

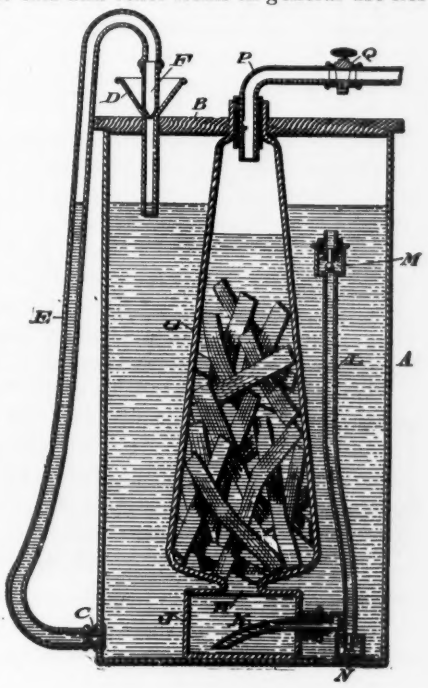
A NEW GENERATOR.

BY EDWARD P. HARRIS.

Received May 27, 1895.

A GREAT many forms of automatic generators for the preparation of such gases as hydrogen, hydrogen sulphide, carbon dioxide, etc., have been proposed, that known as the "Kipp apparatus" being probably most widely used.

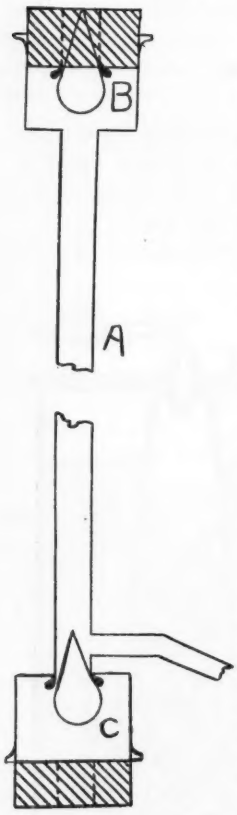
The chief objection to this and other forms in general use lies in the fact that according to their construction the spent acid at the bottom of the reservoir, containing the metallic salts, is used over and over again until it becomes too weak for further action, while plenty of fresh acid remains in the upper part of the reservoir, unable to enter the inner chamber containing the solid material (zinc, iron sulphide, marble, etc.)



The accompanying figures show how this difficulty is removed by a very simple device. The second figure shows the side

tube A enlarged. By mistake the artist has placed the side tube on the wrong side.

The bottom of the inner cylinder is closed and the flow of acid must be through the side tube A. This tube is connected with the lower part of the inner cylinder and is entirely immersed in the acid of the reservoir. At each end is a floating glass valve playing upon a rubber cushion at the end of the tube. When the gas is turned on and the pressure relieved fron the inner cylinder the acid can enter only at B, and when the action is reversed the acid can escape only at C.



Thus, fresh acid from the upper part of the reservoir is always used and the spent acid containing the metallic salts is always deposited at the bottom where it remains, owing to its greater specific gravity. Once set up and charged the only attention this generator needs is the occasional withdrawal of some of the spent acid from the bottom and the addition of an equal quantity of fresh acid through the funnel at the top.

A generator of this description two and a half feet in height has furnished hydrogen sulphide for a class of thirty students in qualitative analysis for eight months, the only attention required being to fill the reservoir three times with acid. The apparatus may be obtained from Queen & Co. in three sizes. The largest size is particularly recommended for generating hydrogen sulphide.

CHEMICAL DEPARTMENT OF THE PENNSYLVANIA MILITARY COLLEGE,
CHESTER, PA.

THE DETERMINATION OF TANNIN BY METALLIC OXIDES.[1]

By William H. Krug.

Received September 6, 1895.

THE following experiments were suggested by a method proposed for the estimation of tannin by Mr. Kerr, associate reporter on tannin, during the progress of the official work for the Association of Official Agricultural Chemists. This method consisted of the percolation of the tannin-bearing liquor through a column of asbestos with which a certain amount of yellow mercuric oxide had been intimately mixed. After making a number of attempts to obtain concordant results, I found it too difficult to secure uniform conditions such as rate of percolation, extent of contact and uniformity in the asbestos layer, and therefore turned to find some other way of using the oxide. It then occurred to me to substitute it for the hide-powder in the ordinary shaker method. During the work I extended the investigation to three other oxides, *viz.*, magnesium, zinc, and lead oxides.

At the beginning it was evident that much more time would be consumed in absorbing the tannin in this manner and a number of preliminary experiments were made to determine this time limit if possible. In all cases when, upon filtration after shaking a certain length of time, it was found that combination was incomplete, the solution was allowed to stand until this was accomplished. It was thus found, that with magnesium and mercuric oxides, it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration.

With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed. These two oxides were, therefore, rejected as requiring too much time, though the analyses made with them, are given below for comparison.

The extract used contained 42.35 per cent. soluble solids, and the diluted liquor used in the analyses, contained two grams of this extract per 100 cc. This diluted extract gave in twenty-

[1] Read at the Annual Meeting of the Association of Official Agricultural Chemists, Sept. 5, 1895.

five cc. as a mean of three determinations, 0.0113 gram ash, containing 0.0006 gram magnesium oxide.

The tannin was determined by the loss insolids, *i. e.*, twenty-five cc. of the filtrate were evaporated on the steam-bath in a weighed dish, dried three hours in a water-bath, and the weight of the residue determined. The difference between this weight and the solids in twenty-five cc. of the original diluted extract, was taken as tannins. The ash determinations were made as a check on the amount of the oxide dissolved during the analysis.

Experiments with zinc oxide.

Method.	Grams ZnO used.	cc. diluted extract used.	cc. of filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Grams ash in residue.	Grams ZnO in ash.
Shaken 4 hours, stood over night	2.0	75	25	0.1095	20.45	0.0125	0.0008
" 4 " " " "	2.0	75	25	0.1174	18.87	0.0147	0.0019
Shaken 4 hours, stood one week	2.0	75	25	0.1049	21.37	0.0095	....
" 4 " " " "	2.0	75	25	0.1029	21.97	0.0103	0.0030
" 4 " " " "	2.0	75	25	0.1029	21.97	0.0100	0.0020

The first two of these analyses gave a faint reaction for tannin, but were run through so as to compare the result with those obtained with other oxides. The low figures indicate incomplete combination. The last three gave no test for tannin when filtered, and agree fairly well. They are low, compared with lead and mercury oxides, and agree better with the results obtained with magnesium oxide. The amount of zinc oxide dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxide is the slow action. The last three analyses were tested every day for a week, before it was found that all the tannin had been absorbed. For this reason zinc oxide would be of no value in a laboratory where the rapid estimation of tannin is desired.

Experiments with lead oxide.

Method.	Grams PbO used.	cc. diluted extract used.	cc. filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Weight of ash from residue.	Grams PbO in ash.
Shaken 3½ hours, stood 2 days	4.0	75	25	0.0738	27.59	0.0111	0
" 3½ " " 2 "	4.0	75	25	0.0754	27.27	0.0092	0
" 3½ " " 2 "	4.0	75	25	0.0706	28.23	0.0105	0

None of these gave a reaction for tannin with ferric chloride. The results were higher than with any other oxide used. The objection to lead oxide is the length of time required for complete combination.

Experiments with magnesium oxide.

Method.	Grams MgO used.	cc. diluted extract used.	cc. filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in residue.	Weight MgO in ash.
Shaken 2½ hours, stood over night	2.0	75	25	0.1134	19.67	0.0209	0.0055
" 2½ " " " "	2.0	75	25	0.1028	21.79	0.0195	0.0042
" 2½ " " " "	2.0	75	25	0.1230	17.75	0.0232	0.0052
" 2½ " " " "	2.0	75	25	0.1246	17.43	0.0247	0.0058
Stood 24 hours with occasional sh'k'g	2.0	75	50	0.2063	21.72	0.0252	0.0074
" 24 " " " "	2.0	75	50	0.2061	21.74	0.0244	0.0076
" 24 " " " "	2.0	75	25	0.1157	19.21	0.0213	0.0044
" 24 " " " "	2.0	75	25	0.1114	20.07	0.0205	0.0038
" 48 " " " "	2.0	75	50	0.1941	22.94	0.0326	0.0064
" 48 " " " "	2.0	75	50	0.1959	22.76	0.0339	0.0070
Shaken 3½ hours, stood over night	2.0	75	50	0.2165	20.70	0.0349	0.0102
" 3½ " " " "	2.0	75	50	0.2191	20.44	0.0355	0.0111
" 3½ " " " "	2.0	75	50	0.2179	20.56	0.0359	0.0115

This table shows that a considerable amount of the oxide is dissolved, and passes into the filtrate, increasing the weight of the residue, and correspondingly lowering the tannin. That this error may be quite considerable is shown by the fact that in almost every estimation, the ash is almost double that found in the original diluted extract. Furthermore, this error does not seem to be constant, so that no correction can be made for it.

Experiments with mercuric oxide (yellow).

Method.	Grams HgO used.	cc. diluted extract used.	cc. filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in residue.	Weight HgO in ash.
Stood 48 hours with occasional sh'k'g	4.0	75	25	0.0833	25.69	0.0070	0
" 48 " " " "	4.0	75	25	0.0829	25.77	0.0077	0
" 48 " " " "	4.0	75	25	0.0829	25.77	0.0071	0
Shaken 1½ hours, stood over night	4.0	75	25	0.0842	25.51	.....	..
" 2 " " " "	4.0	75	25	0.0867	25.01	.....	..
" 3½ " " " "	4.0	75	25	0.0863	25.09	0.0081	0
" 3½ " " " "	4.0	75	25	0.0860	25.15	0.0080	0
" 4 " " " "	4.0	75	25	0.0839	25.57	0.0084	0
" 4 " " " "	4.0	75	25	0.0849	25.37	0.0065	0
" 4 " " " "	4.0	75	20	0.0638	26.41	0.0065	0
" 4 " " " "	4.0	75	20	0.0692	25.05	0.0103	0
" 4 " " " "	4.0	75	20	0.0682	25.29	0.0094	0
" 4 " " " "	4.0	75	25	0.0863	25.09	0.0083	0
" 4 " " " "	4.0	75	25	0.0849	25.37	0.0097	0
" 4 " " " "	4.0	75	25	0.0842	25.51	0.0084	0

The above analyses show that even though the conditions may be varied, fairly concordant results can be obtained with mercuric oxide as long as care is taken to ensure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed, since, when it is reached, the yellow oxide

no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tannin-extract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

THE ESTIMATION OF SULPHUR IN REFINED COPPER.[1]

By G. L. Heath.

Received September 9, 1 95.

SEVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius[1] proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hampe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

[1] Read at the Springfield Meeting.

[2] *Ztschr. anal. Chem.*, 13, 223.

very accurate one, for there are two or three possible sources of error.

1. The existence of the sulphur in different forms.

2. The incomplete removal of all oxygen and other impurities, from the chlorine gas.

3. The occasional formation of a layer of melted chloride, which may prevent the complete evolution of sulphur and combustion of copper.

A third method involves the use of potassium permanganate.

A fourth, and apparently, the most direct and satisfactory one, consists in dissolving ten grams of copper in nitric acid, or in a mixture of nitric with a little hydrochloric acid, and then precipitating the sulphuric acid directly from a hydrochloric acid solution, after removing all the nitric acid by repeated evaporation.

Upon this principle depends the method of H. J. Phillips.[1]

But the writer has repeatedly attempted to test refined copper by the last method, without obtaining any precipitate of barium salt. There should have been at least a trace of precipitate due to sulphur in the chemical reagents.

Though no refining on the large scale has ever produced metal in which a chemist could not find a trace of impurity, yet the best American refined copper of to-day, contains such a minute amount of sulphur, that a very delicate and accurate method is required for its estimation.

In order to test the influence of copper chloride and free hydrochloric acid upon barium sulphate, some experiments were made with solutions of pure copper chloride, and sulphuric acid.

It is a well known fact that certain substances interfere with the precipitation by barium chloride, and that barium sulphate is somewhat soluble in certain acids, and in solutions of copper.

The work of R. Fresenius,[2] F. W. Mar,[4] and others, has indicated that an excess of hydrochloric acid promotes the complete separation of barium sulphate, a conclusion rather contrary to earlier opinions.

[1] *Chem. News*, **62**, and *J. Anal. Appl. Chem.*, **5**, 53.
[2] *Ztchr. anal. Chem.*, **9**, 52 and 62, also Fres. Quant. Anal., Am. Ed. p. 139.
[3] *Am. J. Sci.*, **41**, April 1891, also *J. Anal. Appl. Chem.*, **5**, 278.

Mr. Mar states, as the writer has also noted, that the precipitation of minute quantities of barium sulphate is very much slower than that of large amounts.

Since the barium sulphate is not absolutely insoluble in water or dilute acid, the amount which would remain dissolved by a large volume of solution is appreciable, and cupric chloride may considerably influence the solubility.

As far as the time permitted, the experiments were carried out in two series; those analyses marked *a*, containing but a few drops of free hydrochloric acid, and those marked *b*, *c*, or *d*, about three and a half per cent. by volume of the same acid of 1.20 sp. gr.

Stock solutions were prepared as follows:

a. Standard sulphuric acid—1 cc.=0.00245 gram $BaSO_4$.

b. Cupric chloride solution—100 cc.=10 grams copper.

The solution used for all the experiments (except Nos. 12 *c*. and 12 *d*) was made by dissolving 100 grams of a very pure refined copper in 400 cc. of pure nitric acid, (sp. gr. 1.42), then precipitating the silver with a few drops of hydrochloric acid and filtering it off. The solution was then evaporated to dryness, and the evaporation repeated four times, with the addition of hydrochloric acid each time. The heat was continued until the chloride melted. The salt finally dissolved in water to a clear, faintly acid solution, which was diluted to one liter.

The slight trace of sulphur in the copper, was not any more than that found in the chemical reagents.

Ten grams of the copper yielded, by the author's method, only 0.0017 gram of barium sulphate, and the acids required for solution, gave 0.003 gram, for which allowance was made in the table of results.

c. As a check, some of the same copper was deposited by electrolysis from a nitric acid solution, and the pure plate was then redissolved, and after further treatment, the solution was used for experiments 12*c* and 12*d*, in which one cc. standard sulphuric acid was added to the diluted copper solution.

The measured portions of copper salt, water and acid were placed in beakers and the standard sulphuric acid run in from a

burette. The liquids were heated to boiling, treated with two to five cc. of a saturated solution of barium chloride, stirred, and allowed to stand at the temperature of the room for the number of hours specified in the table.

The precipitates of the tests marked (*b*, *c*, *d*,) were washed first with five cc. of dilute hydrochloric acid, (one part acid to twenty of water) and then with hot water. The ones marked (*a*) were washed with hot water only, and in two or three cases, a trace of copper was not washed out. (See experiments 11*a*, and 15*a*).

At least a few drops of dilute acid should be always used in the first washing by decantation.

The results are tabulated according to the degree of dilution, and the weight of copper in the solution.

TABLE I.

ONE-TENTH GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS SEVENTY CC.

Faintly acid two-tenths free hydrochloric acid.					Strongly acid two and a half cc. hydrochloric acid added.				
	Time in	Gram barium sulphate.				Time in	Gram barium sulphate.		
No.	hours.	Taken.	Found.	Difference.	No.	hours.	Taken.	Found.	Difference.
1*a*	24	0.0025	0.0027	+0.0002	1*b*	24	0.0025	0.0027	+0.0002
2*a*	24	0.0123	0.0127	+0.0004	2*b*	24	0.01235	0.0124	0.0000
3*a*	24	0.04905	0.0489	—0.00015	3*b*	24	0.0491	0.0497	+0.0006

TABLE II.

ONE GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS, 350 CC.

Slightly acid two-tenths cc hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid.				
	Time in	Gram barium sulphate.				Time in	Gram barium sulphate.		
No.	hours.	Taken.	Found.	Difference	No.	hours.	Taken.	Found.	Difference.
4*a*	24	0.0029	0.0026	—0.0003	4*b*	24	0.0029	0.0009	—0.0020
5*a*	24	0.0126	0.0115	—0.0011	5*b*	24	0.0126	0.0101	—0.0025
6*a*	24	0.0495	0.0446	—0.0049	6*b*	34	0.0495	0.0385	—0.0110
6*a*	72	0.0495	0.0490	—0.0005	6*b*	72	0.0495	0.0493	—0.0002
7*a*	72	0.2455	0.2445	—0.0010	7*b*	72	0.2462	0.2500	+0.0038

TABLE III.

TWO AND A HALF GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 350 CC.

Slightly acid two-tenths cc. hydrochloric acid.					Strongty acid 12.5 cc. hydrochloric acid added.				
		Gram of barium sulphate.					Gram of barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
							0.0046	0.0000	—0.0036
8*a*	24	0.0036	0.0007	—0.0029	8*b*	24	0.0936	0.0006	—0.0030
					8*c*	72	0.0036	0.0014	—0.0022
9*a*	72	0.0135	0.0129	—0.0006	9*b*	72	0.0135	0.0128	—0.0007
					9*c*	140	0.0145	0.0131	—0.0014
10*a*	72	0.0502	0.0496	—0.0006	10*b*	24	0.0502	0.0493	—0.0009
					10*c*	72	0.0502	0.0492	—0.0010
					10*d*	140	0.0502	0.0501	—0.0001
11*a*	72	0.2470	0.2505?	+0.0035	11*b*	72	0.2470	0.2486	+0.0016

TABLE IV.

TEN GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 700 CC.

Faintly acid one-half cc. hydrochloric acid.					Strongly acid twenty-five cc. hydrochloric acid added.				
		Gram barium sulphate.					Gram barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
		0.0074	0.0000	—0.0074					
12*a*	24	0.0074	0.0000	—0.0074	12*b*	24	0.0074	0.0000	—0.0074
					12*c*	140	0.0057	0.0005	—0.0052
					12*d*	"	0.0057	0.0004	—0.0053
13*a*	72	0.0170	0.0102	—0.0018			0.0165	0.0014	—0.0151
					13*b*	24	0.0165	0.0013	—0.0153
14*a*		lost			13*c*	72	0.0165	0.0051	—0.0114
					14*b*	24	0.0540	0.0502	—0.0038
					14*c*		0.0540	0.0400	0.0140
15*a*	72	0.2509	0.2551?	+0.0047	15*b*	24	0.2500	0.2389	—0.0111
						72	0.2500	0.2436	—0.0064
						140	0.2500	0.2474	0.0026

The results, given in Table I., show that if the total volume of a solution is not over 100 cc. the barium sulphate is completely precipitated, whether the liquid is strongly acidified or not.

Table II: If the volume of the solution is increased to 350 cc. and the copper to two and a half grams, the precipitation is complete, even then, under the given conditions, in 72 hours with the exception of the analysis containing but a trace of sulphuric acid.

Tables III and IV: In the presence of as much as ten grams of copper in solution, the deposition becomes very slow indeed, as the results prove, and the strongly acidified solutions, at least retain appreciable amounts of barium sulphate.

Since the solubility of barium sulphate varies according to the conditions somewhat, the figures given by Fresenius, F. W. Mar, and others would not express the true effect of the water and dilute hydrochloric acid if the conditions of acidity, temperature, dilution, etc., were not the same. So a few experiments were made to determine the solvent effect of the water and acid alone.

Analyses 16-20 indicate that a part at least of the deficiency noted in the other tables is due to the solubility of the precipitate in the large volume (700 cc.) of dilute acid.

TABLE V.

No.	cc. of hydrochloric acid.	Temperature during settling.	Total volume.	Time in hours.	Gram barium sulphate. Taken.	Found.	Difference.
16	25	20° C.	700	48	0.0025	0.0008	—0.0017
17	25	20° C.	700	48	0.0123	0.0086	—0.0037
18	25	20° C.	700	48	0.0490	0.0470	—0.0020
19	2 cc. + 5 grams ammonium chloride.	75° C.+	70	3	0.0490	0.0487	—0.0003

Fresenius[1] states that 1,000 parts of cold hydrochloric acid containing 3 per cent. dissolve 0.06 parts $BaSO_4$.

Other experiments proved, however, that if a solution be kept at a temperature above 75° C., after the addition of barium chloride, the separation of barium sulphate is far more rapid and complete.

Cupric chloride appears to retard the deposition, especially when strongly acidified.

Direct precipitation in a moderately acid solution of this salt is determined to be sufficiently accurate for mattes and crude copper, but the separation of minute amounts of barium sulphate, from a very large volume of chloride solution, is too uncertain to permit the use of such a method for the detection and estimation of traces of sulphur in the best modern refined copper.

[1] F. Quant. Anal., 1st Am. Ed., p. 139, from Anal. Chem., 9, 62.

In 1889 the late Dr. L. M. Norton and the author of this paper devised and adopted a simple method, which has been improved by the latter, and has given very accurate results.

The complete precipitation of the barium sulphate is made possible in every case by first removing the copper electrolytically and then treating the solution as in the following scheme:

Take for analysis sufficient copper to yield a weighable amount of barium sulphate—ten grams will usually be enough.

Dissolve in a large beaker, placed over an alcohol flame, by means of a mixture of 60 cc. nitric acid (1.42 sp. gr.) and 15 cc. of hydrochloric acid (1.20 sp. gr.).

When dissolved, raise the lamp wick and evaporate nearly to dryness, then evaporate again after adding 50 cc. strong nitric acid.

Repeat this operation with another portion of the same acid, then redissolve in 300 cc. of water, and add a little nitric acid if a trace of basic salt remains undissolved.

The addition of hydrochloric acid and the consequent evaporation with nitric may be dispensed with, if experiment shows that nitric acid alone will oxidize all the sulphur in the class of material operated upon.

Next, pour the liquid through a small filter into a 700 cc. beaker and dilute with distilled water to 600 cc. or more.

Introduce as a negative electrode a large cone, or as is more convenient, a sheet of platinum, 4 by 5 inches.

Any wire or small piece of platinum foil will serve as a positive electrode.

Cover the beaker with glass and connect the electrode, preferably with an Edison incandescent lamp circuit.

The current from two sixteen candle-power lamps, coupled in parallel, will deposit the copper in one night.

When the liquid is colorless, or nearly so, remove the electrodes and wash them with distilled water, allowing the water to run into the main solution.

Pour off the liquid, if clear, from any bits of spongy copper, washing these on a small filter.

In order to prevent the escape of any sulphuric acid during subsequent evaporation, add, at this point, one-tenth gram dry,

pure sodium carbonate, (or a half gram for crude copper).

Evaporate the solution to dryness, as rapidly as possible without loss, in a No. 3 or No. 4, porcelain casserole. An alcohol lamp should be used, and the dish protected from dust. The evaporation may be completed on the water-bath, but if the dish is covered near the end of the operation and the flame regulated, there need be no loss by spattering, though the liquid be taken to dryness over the lamp. As soon as the salts in the dish are dry, heat the covered casserole quite strongly, with the lamp held in the hand, until the acid ammonium nitrate suddenly volatilizes, and then allow it to cool.

At this point is the only danger of loss of sulphur, and the heat should be just high enough to volatilize the nitrate. This heating may possibly be omitted if there is but a trace of ammonium nitrate in the dish. (See experiment 19).

Add to the residue, ten cc. strong hydrochloric acid and five cc. water, and evaporate to dryness on the water-bath. Repeat the process and then add one cc. of strong hydrochloric acid, add fifty cc. of water and dissolve, filter into a small beaker and wash the filter with hot water.

If the copper is known to be high in sulphur, the solution may be diluted to 150 cc. or more.

The only impurity of copper which might interfere with this method is lead. If lead is present, it will mostly remain in solution and be deposited on the plate, but if any lead sulphate remains on any of the filters, they must be boiled with a little solution of pure sodium carbonate, the solution filtered, and the sulphuric acid recovered from the acidified liquids as barium sulphate.

Heat the solution of sodium sulphate to boiling, precipitate with a slight excess of barium chloride, and allow the precipitate to settle twenty-four hours, unless the results are desired at once, in which case the precipitation may be completed inside of three hours, by keeping the liquid at a temperature not less than 75° C. during that time.

The acids and distilled water, used in the analysis, should be measured, and a blank analysis carefully made by evaporating with the pure soda, and the trace of barium sulphate deducted

from that of the analysis proper. Exp. 20–22 are three comparative analyses from the writer's note-book.

TABLE VI.

COPPER ANALYSIS.

		Per cent. sulphur.		Per cent. sulphur.
20	Direct precipitation	0.0000	Author's method	0.0023
21	" "	0.6000	" "	0.6500
22	" "	0 to 0.0050	" "	(1) 0.0112
22	Chlorine method	0.0189?		(2) 0.0094

It is evident that the method just detailed, is extremely well adapted to the analysis of refined copper.

The sulphur in the metal is brought into solution, and finally precipitated in a pure condition without loss, and a blank analysis is possible under the same conditions. The difference between the two results, expresses the true quantity of sulphur present.

Another chemist stated sometime ago that he, also, had been obliged to try a similar plan. The author has, however, worked out the foregoing process in its improved form independently, and in presenting this standard method, desires to express his indebtedness to the gentleman who has so kindly consented to read the paper before the assembly.

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.[1]

BY LYMAN F. KEBLER.

Received September 9, 1895.

THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behavior with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schlössing[2] proposed the method and applied it to the titration of nicotine with a view of establishing its equivalent; using sulphuric acid and litmus in his work. Sixteen

[1] Read at the Springfield meeting.

[2] *1847, Comp. rend.*, **23**, 1142; *1847, Ann. Chim. Phys.* [3], **19**, 230; Chem. Gaz., 5, 41; Am. J. Pharm., **19**, 68.

years later the work was taken up by Wittstein,[1] who was followed by F. M. Brandl,[2] Liecke,[3] Kosutany,[4] and G. Dragendorff.[5] Up to this time nicotine and conine were the only alkaloids operated on, and litmus the only indicator employed. In 1879 L. van Itallie[6] extended the work to several other alkaloids, using lacmöid as indicator. A. W. Gerrard[7] a few years later employed litmus and phenolphthalein in titrating the alkaloids of belladonna. From the contributions of O. Schweissinger,[8] who used cochineal as indicator, and those of E. Dieterich[9] and P. C. Plugge[10] we may ascribe the impetus which the titration of alkaloids with volumetric acid solutions received at the beginning of the present decade.

The method had been gaining ground rapidly when several most valuable communications appeared by C. C. Keller,[11] of Zürich, since which great improvement has been made.

In volumetric analysis, the first question demanding attention is a suitable indicator or delicate end reaction.[12] The object of this communication is to present the results of a study of five indicators in titrating alkaloids, thinking perhaps it may be of some service in formulating systematized methods of analysis in alkaloidal chemistry. The discordant results of analysis often obtained by different chemists operating on the same sample are greatly to be regretted. It is the writer's opinion that

[1] *1862*, Vierjahrschr. prakt. Pharm., **11**, 351.

[2] *1864*, Vierjahrschr. prakt. Pharm., **13**, 322.

[3] *1865*, Mittheilungen des hannov. Gew-Ver., p. 160; Ding. poly. J., **178**, 235; Polyt. Notizbl., No. 20; Ztschr. anal Chem., **4**, 492.

[4] *1873*, Kosutany, Anal. Bestim. einiger Bestandth. d Tabakspflanze. Diss. Altenburg, Hungary.

[5] *1874*, Chem. Werthbestim., p. 42 and 55; see also Plant Analyses. *1884*, Eng. Ed., pages 63 and 188.

[6] *1879*, Nederland. Tydschr. v. Pharm., Jan; *Analyst*, **14**, 118.

[7] *1882* and *1884*, Year-Book of Pharm., p. 401, 447.

[8] *1886*, Pharm. Centralhalle, **27**, 492.

[9] *1887*, Pharm. Centralhalle, **28**, 21; Pharm. J. Trans. [3], **17**, 888; *Am. J. Pharm.*, **59**, 179.

[10] *1887*, Arch. d. Pharm. [3], **25**, 45, 49; J. de Pharm. et de Chim. [5], **15**, 571; *Ber. d. chem. Ges.*, **20**, 148; *J. Chem. Soc.*, **52**, 621.

[11] *1892*, Schweiz., Wochenschr. f. Chem. u. Pharm., **30**, 501, 509; *Am. J. Pharm.*, **65**, 78. *1883*, Schweiz., Wochenschr. f. Chem. u. Pharm., **31**, 473; Ztschr. Oesterreich- Apoteker., **47**, 563, 586; *Am. J. Pharm.*, **66**, 42.

[12] Alkaloids, generally, are neutral to phenolphthalein, consequently it cannot be employed in titrating alkaloids directly. It is available for indirect titrations, *i. e.*, estimating the amount of acids combined with an alkaloid in its neutral salts.

the discrepancies are chiefly due to differences in *modus operandi*, to defective apparatus, and, in volumetric analysis, to different end reaction tints arbitrarily assumed by each worker.

In order to eliminate the factors of uncertainty as completely as possible the methods of operation were carefully written out and closely adhered to in all the work. The burettes and a pipette were carefully calibrated in order to ascertain the necessary factor for correction. The method of calibration was as follows: each burette and pipette was exactly filled to the zero mark with distilled water, at 15° C. and ten cc., delivered into a tared weighing flask and weighed, then the next ten cc. were treated in the same manner, and so on until the entire capacity of each was tested. A glass-stoppered cylinder was also standardized. All efforts to standardize a liter flask were thwarted. A large balance sufficiently sensitive to do the work satisfactorily could not be found.

In titration the personal equation plays an important part. Authorities are not agreed on end reaction tints, each operator relying on his own judgment. The writer thinks it correct to titrate to the point where a different color from the initial color is developed. In order to obtain standard end reaction tints for alkaloids it will be necessary to prepare some absolutely pure alkaloid; treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid color reaction. For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared.

In this work the writer titrated from acid to alkaline solutions as follows: Brazil wood, from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish-red; haematoxylin from yellow to brown-orange; litmus from red to onion-red, and methyl orange from red to straw-yellow.

The indicator solutions were prepared according to the most approved processes. Cochineal and litmus were prepared according to the specifications of Sutton's Volumetric Analysis, sixth edition. Phenolphthalein, one gram dissolved in one liter of fifty per cent. alcohol. Haematoxylin, well crystallized, one

gram dissolved in 100 cc. of strong alcohol. The method best suited for preparing the Brazil wood solution, is to place three grams of the wood into a casserole, add ten cc. of distilled water, boil gently for a few minutes, cool, and filter. A freshly prepared solution has given the writer the most satisfactory results. Methyl orange, one gram dissolved in one liter of distilled water. Considerable difficulty was experienced in obtaining even a fairly satisfactory product of methyl orange. The method proposed by Mr. B. Reinitzer[1] for preparing the litmus solution did not come to the writer's notice until considerable work had been done with the solution prepared as above.

In titration the following quantities of the several indicators were employed: methyl orange, Brazil wood, cochineal, and phenolphthalein, five drops each; litmus ten drops and haematoxylin three drops.

The standard solution employed in this investigation, from which the exact strength of the other volumetric solution was determined, was a solution of normal sulphuric acid. This solution was prepared from data obtained by the several methods; titration against pure anhydrous sodium carbonate, using the above indicators; precipitation as barium sulphate and Weinig's[2] process. After some experimentation, it was found that Weinig's method gave the most satisfactory results. The method is simple and yields very concordant results. The following are the data obtained from an approximately normal sulphuric acid solution with the above methods:

Indicators and methods.	No. of cc. of acid solution required per ten cc. of normal sodium carbonate.	Grams of SO_3 in ten cc. of the acid solution.
Brazil wood	9.50	0.4211
Haematoxylin	9.54	0.4192
Cochineal	9.50	0.4211
Litmus	9.50	0.4211
Methyl orange	9.50	0.4211
Phenolphthalein	9.45	0.4216
Weinig's method	....	0.4247
Barium sulphate method	....	0.4200

Due precaution was taken to boil the solution thoroughly with

[1] *1894*, Ztschr. angew. Chem., 547, 573; Chem. News, 70, 225, 239, 249.
[2] *1892*, Ztschr. angew. Chem., 204; Analyst, 17, 99.

the indicators requiring it. With solutions of the above strength it was impossible to detect any difference in the sensitiveness of most of the indicators.

With the normal sulphuric acid solution a normal solution of pure potassium hydroxide was standardized. From the normal sulphuric acid solution and normal alkaline solution there were prepared, respectively, a decinormal acid solution and a centinormal alkaline solution. The two solutions thus prepared were carefully titrated against each other, employing the above indicators with the following results:

Indicators.	No. of cc. of normal sulphuric acid.	No. of cc. of centinormal KOH required per ten cc. of decinormal H_2SO_4.	
		LaWall.	Kebler.
Phenolphthalein.....	10	101.80	102.00
Brazil wood.....	10	99.56	100.00
Cochineal.....	10	100.58	99.80
Haematoxylin	10	99.76	100.00
Litmus	10	99.97	99.60
Methyl orange	10	92.67	98.53

My associate, Mr. LaWall, took up a portion of the work, which he executed independently, using, however, the same solutions and apparatus that the writer employed. The above, and all subsequent results, are the average of duplicate, triplicate or more titrations.

The titration of pure alkaloids, as found in the market, was next undertaken. With quinine and codeine the following method was used: two grams of the alkaloid were placed in the cylinder, dissolved in alcohol, and diluted up to 100 cc. with alcohol. To ten cc. of this solution and the requisite quantity of indicator contained in a suitable beaker, the decinormal acid solution was added to slight excess, agitated, allowed to stand a few minutes, the sides of the beaker well washed down with distilled water, adding about forty cc., and the excess of acid titrated back with the centinormal alkaline solution.

With alkaloids not freely soluble in alcohol, the following procedure was adopted: two grams of the alkaloid were placed into a 200 cc. beaker, seventy-five cc. of decinormal acid added, the contents of the beaker warmed on a water-bath and occasionally agitated until the alkaloid was dissolved. The beaker

and contents were then cooled, the contents transferred to a 100 cc. cylinder, the beaker carefully rinsed with several successive portions of water, transferred to the 100 cc. cylinder and finally made up to 100 cc. with water. Each ten cc. contained two-tenths of a gram of alkaloid and seven and a half cc. of decinormal acid solution. After adding the requisite amount of indicator to ten cc. of the alkaloidal solution and diluting up to about fifty cc., the excess of acid was carefully retitrated. Two or more titrations were made in every case, with the same solution and indicator, by adding to the solution just finished, another portion of the decinormal acid solution and retitrating with the centinormal alkaline solution, taking finally the average reading.

The above methods of titration and preparation of solutions were employed with several pure alkaloids. The results are tabulated below.

	Quinine.		Strychnine.	Morphine.	Codeine.
Indicators.	LaWall.	Kebler.	Kebler.	Kebler.	Kebler.
Brazil wood.....	99.90	101.97	99.36	98.93	95.75
Cochineal	105.56	102.54	103.20	99.08	97.09
Haematoxylin	99.81	103.37	100.03	98.17	95.90
Litmus	101.80	103.55	103.54	98.93	96.38
Methyl orange.....	....	123.27	104.21	100.59	98.11

The number of times the analyst is requested to investigate the purity of refined alkaloids is comparatively small, but the crude alkaloids claim a greater share of his time and attention.

The next step was to investigate the adaptability of the above process to crude morphine and crude cocaine. The results are as follows:

	Crude morphine.		Crude cocaine.
Indicators.	LaWall.	Kebler.	Kebler.
Brazil wood.....	99.23	98.47	95.90
Cochineal.....	100.14	99.53	97.11
Haematoxylin	99.08	97.59	95.74
Litmus	99.50	98.93	96.82
Methyl orange.....	102.10	100.02	100.14

With the same crude morphine the ash method yielded 97.59 per cent., the lime-water method 98.22 per cent., and the absolute alcohol method 98.33 per cent. of pure morphine.

A complete analysis was made of the crude cocaine to ascer-

tain how nearly the titrations corresponded with the gravimetric process of Dr. Squibb.[1]

	Per cent.
Moisture	0.405
Cocaine nearly pure	97.300
Material soluble in ether	0.100
Material insoluble in ether	1.810
Loss	0.385
Total	100.00

Notwithstanding the fact that crude alkaloids claim considerable attention on the part of the analyst, yet only a few are found already extracted on the market. It generally happens that the operator is requested not only to determine the amount of pure alkaloids, but also to extract them from their natural sources. For this purpose the writer employed a modification of Keller's process. The method is as follows: place ten grams of the dry drug into a 250 cc. flask, add twenty-five grams of chloroform, seventy-five grams of ether, stopper the flask securely, agitate well for several minutes, add ten grams of ten per cent. ammonia water, then agitate frequently and during one hour. On adding five grams more of ten per cent. ammonia water and shaking well, the suspended powder agglutinates into a lump, the liquid becomes clear, after standing a few minutes, and can be poured off almost completely.

1. When the mixture has completely separated, pour off fifty grams into a beaker, evaporate the solvent on a water-bath, add ten cc. of ether, and evaporate again. Dissolve the varnish-like residue in fifteen cc. of alcohol, with heat, add water to slight permanent turbidity, the requisite quantity of indicator and an excess of the acid solution; retitrate with the centinormal alkaline solution.

2. When the mixture has completely separated pour fifty grams into a separatory funnel, treat at once with twenty cc. of acidulated water. After thorough agitation and complete separation remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with fifteen cc. of slightly acidulated water. The acidulated water

[1] Ephemeris, 3, 1171.

in the second separatory funnel is rendered alkaline with ammonia water, the alkaloid removed successively with twenty cc., fifteen cc., and fifteen cc. of a mixture of three parts (by volume) of chloroform and one part of ether. Collect the chloroform-ether mixture in a tared beaker and distil off the solvent. The varnish-like residue is twice treated with eight cc. of ether, evaporated on a water-bath and dried to constant weight on the water-bath. The varnish-like residue is next dissolved in fifteen cc. of alcohol and treated as in (1) above.

Nux vomica and ipecac root were treated according to processes (1) and (2); belladonna leaves according to process (2). The results are as follows:

	Per cent. of alkaloids in nux vomica by process (1).		Per cent. of alkaloids in nux vomica by process (2). Gravimetrically.		Per cent. of alkaloids in nux vomica by process (2). Volumetrically.		Per cent. of alkaloid in ipecac root by process (1.)	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler
Brazil wood.....	2.04	2.58	2.94	3.00	2.37	2.37	2.46	2.54
Cochineal	2.64	2.69	2.86	3.10	2.42	2.39	2.59	2.49
Haematoxylin ...	2.18	2.24	2.88	3.11	2.23	2.27	2.48	2.54
Litmus	2.38	2.34	2.93	3.05	2.55	2.37	2.55	2.57
Methyl orange...	3.02	3.64	2.93	3.02	2.65	2.61	2.95	3.30

	Per cent. of alkaloid in ipecac root by process (2). Gravimetrically.		Per cent. of alkaloid in ipecac root by process (2). Volumetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Gravimetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Volumetrically.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood.....	2.58	2.60	2.36	2.35	0.26	0.20	0.19	0.15
Cochineal	2.63	2.68	2.52	2.33	0.28	0.20	0.24	0.14
Haematoxylin ...	2.58	2.68	2.35	2.33	0.27	0.22	0.21	0.13
Litmus	2.62	2.60	2.40	2.25	0.24	0.18	0.20	0.15
Methyl orange...	2.66	2.63	2.89	2.61	0.25	0.20	0.23	0.20

According to the well-established method of Messrs. Dunstan[1] and Short, the nux vomica examined contained 2.89 per cent. of crude alkaloid. On carefully titrating this crude product with a volumetric acid solution, 2.12 per cent. of pure alkaloid was indicated. Cochineal was used as an indicator. These figures show that this method produces an alkaloid residue containing a smaller percentage of pure alkaloid than that obtained by Keller's process.

[1] *1887*, Pharm. J. Trans. [3], **13**, 665.

From the results embodied in this paper it can safely be concluded that methyl orange cannot be numbered with the indicators suitable for titrating alkaloids. With centinormal, fifth decinormal and other solutions of various strengths it fails to give satisfactory results. Notwithstanding the sensitiveness claimed for it, the writer believes that its days, as an ideal indicator, are numbered. Even Professor Lunge, the staunch advocate of methyl orange, has admitted that a properly prepared solution of litmus is quite superior to this indicator, in inorganic estimations.

A solution of litmus prepared according to the directions herein employed is quite unsatisfactory for delicate titrations. The method proposed by Reinitzer promises to be better suited.

Of the indicators thus far considered, haematoxylin, Brazil wood, and cochineal give very promising results. Haematoxylin justly claims first place and Brazil wood the second. Other indicators will be considered in due time.

As stated above, the prime object of this investigation is to ascertain what indicators are best adapted to the titration of alkaloids; but in order to determine how reliable the results were, gravimetric determinations necessarily formed a part of the work.

When it is remembered that not only do analytical methods contain inherent limitations, but also that each operator possesses a positive or a negative equation of error, the reader will undoubtedly concur with the writer that the results are very satisfactory. Attention must again be called to the fact that the work was conducted under precisely the same conditions.

As would naturally be expected, the amount of alkaloid obtained by process (2) is smaller than that secured by process (1). A small per cent. of the alkaloid may be lost during the process of extraction. The small amount of coloring-matter possibly vitiates the results, or perhaps some non-alkaloidal substance increases the yield in process (2).

From the hundreds of assays made by the author, he feels justified in stating that all of the gravimetric processes yield products containing considerable non-alkaloidal matter, and hopes that the day is not far distant when all gravimetric results

will at least be supplemented by volumetric methods, if not displaced by them.

THE MORE VALUABLE LITERATURE ON INDICATORS DURING THE LAST TWO DECADES.

1877. E. Luck: Ztschr. anal. Chem., **16**, 332.
1880. A. Baeyer: Ann. Chem. (Liebig) **202**, 68.
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1882. G. Tobias: Ber. d. chem. Ges., **15**, 2452.
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1883. H. Beckurts: Pharm. Centralhalle, **24**, 333; Abstr., Ber. d. chem. Ges., **17**, 3073.
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1883. R. T. Thomson: Proc. Phil. Soc. Glasgow, **15**, 63, 194; (1884) Chem. News, **49**, 32, 38, and 119.
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1885. G. Lunge: Ber. d. chem. Ges., **18**, 3290.
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1891. J. Lüttke: Apoth. Ztg., **7**, 643; Ztschr. anal. Chem., **31**, 692.
1893. M. B. Breed: J. Frank. Inst., **135**, 312; J. Anal. Appl. Chem., **7**, 204.
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1894. B. Reinitzer: Ztschr. angew. Chem., 547, 573; Chem. News, **70**, 225, 239, 249.
1894. G. Lunge: Ztschr. angew. Chem., 733.
1894. W. Schafer: Apoth. Ztg., **9**, 839; Abstr., Analyst, **20**, 37 (1895).

NEW BOOKS.

ELEMENTS OF MODERN CHEMISTRY. By CHARLES ADOLPHE WURTZ. Fifth American Edition. Revised and enlarged by Wm. H. Greene, M.D., and Harry F. Keller, Ph.D. 12 mo. pp. 788. Philadelphia: J. B. Lippincott & Co., 1895.

On the whole, this is a very good text-book, well adapted to the needs of high schools and general use in colleges, as its popularity proves. From the reviewer's standpoint, however, it possesses two distinct faults. First, the disproportionately large space given to organic chemistry. This part of the subject is full of very important information, but it has taken on too much of the style of a dictionary and too little of the analytical method of a treatise. The result is 360 pages of material which by judicious generalization should have been condensed to half that amount, in order to correspond in size to the rest of the book. For instance, two pages are given to describing succinic acid, and yet barely a single page each to barium, strontium or cadmium, with all their compounds; the derivatives of urea take five pages, while the subject of chemical energy and thermochemistry is disposed of in just half that space. Secondly, the lack of true inductive reasoning in establishing the probability of the atomic theory. The introductory pages on chemical theories and laws contain the "Articles of Faith" of the atomic theory, very clearly stated, but it must be said that the theory itself is virtually taken for granted. For instance, speaking of forming ferrous sulphide by melting iron filings and sulphur together, it is said, "After cooling it is perfectly homogeneous, neither iron nor sulphur can be recognized. Both have disappeared as such." This is perfectly true, and according to experience. But, a few lines further we have: "It cannot be admitted that these two substances are confounded in the molecule, or that the effect of the combination of sulphur with iron is an interpenetration of the two bodies, so intimate that they both disappear in what might be called a homogeneous mixture." The student might very naturally inquire why it could not be admitted, since such an admission would coincide so well with the facts as far as we know them; and the only answer that

could be made would be, "It would not agree with the atomic theory." The student might well say, "So much the worse for the theory!"

We note the absence of thermochemical data, the most important of which might well serve for illustrating the general relations of the elements to each other and to the acids. In the chapters describing the metals and their compounds, many of the simple blowpipe tests for identifying the elements are omitted, and for some common elements no qualitative tests at all are given. The table of the melting-points of the metals needs revision. The electrolytic method of refining copper cannot now be spoken of as expensive. The mineral Edisonite, spoken of as a form of titanic oxide, has been proved to be rutile. Among the methods of manufacturing caustic soda, bleaching powder, and potassium chlorate, the electrolytic methods are not mentioned—as they surely should be.

On the other hand, the numerous revisions to which the text has been subjected have ensured the almost certain accuracy of the facts presented and the absence of mistakes. The revision up to date has been done in a way which reflects great credit on the revisers. Granted that the teacher will remedy the faults first spoken of by cutting down much of the detail of the organic chemistry and presenting the atomic theory in a more logical manner, and we may pronounce the book the best elementary text-book of chemistry of the year.

JOSEPH W. RICHARDS.

JUSTUS VON LIEBIG, HIS LIFE AND WORK. By W. A. SHENSTONE. 12mo. pp. 219. $1.25. New York: Macmillen & Co.

Liebig's personality was an interesting one. His life was one of earnest purpose and hard work. He was a many-sided man, and his influence was felt in many directions. In investigation, as a man of affairs and as a popular teacher, Liebig's work has been of use to his kind. Of the brilliant chemists of his day—Graham, Dalton, Wöhler and Dumas, among others—his career is the most interesting. Liebig's work began in Gay Lussac's laboratory where in connection with his work on the fulminates he discovered isomerism. In 1824 he went to Giessen, and in 1852 to Munich. "Liebig was essentially a pioneer in science.

In the course of his life he took the lead in no less than four great departures. The first was in organic chemistry, the second and third in the application of chemistry to agriculture and physiology, the fourth * * was the outcome of his labors as a teacher. His work, like that of other pioneers was, of course, not always correct in all points of detail. But it had all the greater merits of good pioneering work in a most marked degree. It almost always pointed the right way, and its remarkable influence in determining the direction of subsequent research has been singularly permanent.'' To this may be added that he was a virile man, vigorous and trenchant in debate, but honoring truth above all things, and willing to acknowledge his errors—and several times he was in the wrong.

Professor Shenstone has given us a very interesting and lucid account of his life and his work.

E. H.

NOTE.

Determination of Acetic Acid in Vinegar.—Dr. B. F. Davenport wishes to call attention to his article on this subject printed in the *Journal of Analytical Chemistry*, **1**, 4, in view of the fact that Prof. Leeds' attention had apparently not been called to it before writing the article printed in the September number of this journal, p. 741.